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Diode Laser Diagnostics for Gas Species and Soot in Large Pool Fires

LDRD Project Final Report

Christopher R. Shaddix, Sarah W. Allendorf, Gary L. Hubbard, David K. Ottesen,
and Louis A. Gritzso

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DIODE LASER DIAGNOSTICS FOR GAS SPECIES AND SOOT IN LARGE FIRES

LDRD Project Final Report

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Abstract

The thermal hazard posed by a fire to a weapon or other engineered system is a consequence of combined radiation and convection from high-temperature soot and gases. The development of advanced, predictive models of this hazard requires detailed knowledge of the transient chemical structure and soot distributions within real-scale fires. At present, there are no measurements, and hence limited understanding, of transient gaseous species generation and transport in large, fully turbulent fires. As part of a Laboratory Directed Research and Development (LDRD) project to develop such an experimental capability, near-infrared tunable diode laser absorption spectroscopy (TDLAS) has been identified as the most promising diagnostic technique for making these measurements. In order to develop this capability, significant efforts were applied to choosing optimal species and transitions for detection, to developing an effective multiplexing strategy for several lasers undergoing wavelength modulation spectroscopy with fast laser ramp scans, to developing a methodology for multipassing the TDL beams across a small probe volume, and finally, to designing a water-cooled, fiber-coupled probe for performing these measurements locally within large pool fires. All of these challenges were surmounted during the course of this project, and in the end a preliminary, unique dataset of combined water vapor, acetylene, and soot concentrations was obtained from a 1-m diameter JP-8 pool fire.

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Introduction

This report documents a Laboratory Directed Research and Development (LDRD) project with the aim of developing a diagnostic technique for simultaneous measurements of major gas species concentrations and soot properties with high spatial and temporal resolution in large fires. It was proposed to use near-infrared tunable diode lasers (TDLs) for the gas species measurements and a fixed-wavelength diode laser for soot concentration measurements, together with 2-color pyrometry for soot temperature measurements. A number of significant technical hurdles were recognized in the application of TDLs for species measurements in this environment, whereas the so-called “3-color” soot diagnostic had already been developed and demonstrated in large fires (Gritz et al., 1998a). Consequently, the focus of the project was on addressing the TDL requirements for the desired measurements. In the course of designing a suitable optical configuration for the TDL measurements, it became imperative to modify the traditional, relatively bulky optical configuration applied for the soot diagnostic, so this diagnostic was redesigned to minimize its required optical access. This project evolved from literature reviews and spectroscopy calculations to bench-scale instrumentation tests to laboratory buoyant diffusion flame testing and finally to a single series of large-scale (1-m diameter) JP-8 pool fire tests at Sandia’s FLAME facility in Albuquerque. While not strictly following a chronological order, this report traces a similar path from the theoretical and analytical underpinnings of various design decisions to component tests and finally to integrated system testing.

This project is motivated by the need for advances in fire diagnostics to improve both the phenomenological understanding of large fires and the development of high-fidelity computer codes for the prediction of fire effects. Sandia National Laboratories is specifically interested in making accurate predictions of heat transfer from large pool fires that may occur in certain accident scenarios involving the transport of critical engineered systems or nuclear materials. Previous experimental research has demonstrated that the structure and heat transfer characteristics of these fires vary significantly with a number of factors, including ground plane geometry, wind velocity, object size and location (relative to the pool and the wind vector), pool size, and fuel type. This large, coupled set of variables that influence fire behavior, combined with the high cost associated with conducting large-scale fire tests, has motivated a focus on conducting fewer, better instrumented fire experiments and on developing a high-fidelity computational fluid dynamics (CFD) code for fire simulations that utilizes massively parallel computer architecture (the ASCI Fuego project). Advanced diagnostics that improve the knowledge of the local physics and chemistry of fires are desired both to improve our phenomenological understanding of fire behavior and to provide quality measurements with the correct spatial and temporal resolution for direct comparisons with the predictions from advanced fire simulations.

Because of the relatively low velocities (especially near the pool surface), high temperatures, and high soot loadings in pool fires of practical transportation fuels, the predominant mode of heat transfer to significantly sized objects that are engulfed or adjacent to these fires is thermal radiation from soot (Gritz et al., 1998b). Radiation from infrared-active gaseous species produced in fires, especially carbon dioxide and water vapor, may also be an important heat transfer mechanism in some situations, especially when the fuel source is an alcohol or similarly lightly-sooting fuel. Furthermore, measurements of the heat flux at the center of large pool fires show a significant decrease relative to those in the outer annulus of the fires (Gritz et al., 1998b). This decrease must either be from radiative absorption by cold soot in the interior of the fire or from gas-phase radiative absorption, presumably by the mix of hydrocarbons that probably exists in this region.

These considerations form the backdrop to any consideration of important measurement technologies to apply in large fires.

State-of-the-Art of Fire Diagnostics

The list of measurement technologies that have been successfully applied to large fires pales in comparison to the number and sophistication of the techniques that have been applied to smaller-scale, non-sooting flames, as are often investigated in combustion research laboratories. Techniques relying on high-intensity lasers typically fail in the sooty diffusion flames that are characteristic of practical fires, due to strong, broadband incandescence from laser-heated soot, as well as broadband fluorescence from laser-excited polycyclic aromatic hydrocarbons (PAH). Furthermore, the short light extinction lengths in large, sooty fires precludes the use of any technique relying on external laser sources and external imaging of the laser-flame interaction, as is typically done in laboratory flames. A brief discussion of the major diagnostic techniques that have been applied to large fire measurements is presented in the following:

Cameras/Video

Video and still cameras are often used in fire research to benchmark overall fire behavior and establish the overall fire size and shape. In addition, video cameras can readily be used to determine the characteristic "puffing" frequency. High-resolution cameras can be used to determine the extent of flame wrinkling in local regions on the edge of large fires and to give information on flame thickness (e.g., Tieszen et al., 1996). For the most part, broadband video and still cameras have been used, limiting the information content to soot-containing regions of the fire and giving a strong weighting to the hottest soot. Occasionally, infrared-sensitive cameras have been used to image fires in a manner that is more reflective of the radiant intensity within the fire, but these detectors have substantially poorer spatial definition, limiting their usefulness in determining fire structure.

Thermocouples

Thermocouples are certainly one of the most ubiquitous measurement instruments for large fire research, because of their low cost, ruggedness, and ease of application, as well as the fundamental importance of the fire property that they measure – the local temperature. The local gas and soot temperatures are critical for denoting the presence or absence of active flame sheets at a given location in a fire and also control both the convective and radiative heat transfer to embedded or adjacent objects. Unfortunately, the use of thermocouples in fire environments is fraught with uncertainty in interpreting the measured values. Both radiative heat transfer between the thermocouple and the surrounding media and thermal inertia effects from using finite thickness wires contribute to errors in the derived measurements that are difficult to quantify. The thermal inertia effect results in measurements that have poor temporal response in most practical applications. For example, 1/16" (1.6 mm) sheathed thermocouples are commonly used in large fire tests, and have characteristic response times of 1-4 s (Gregory et al., 1989; Schneider and Kent, 1989). The use of bare or thin-coated fine-wire thermocouples reduces the response time significantly (e.g. 5-mil or 127 μm thermocouples have a response time of ~ 0.1 s), but at a cost of ruggedness and reliability. In comparison, buoyant flames and fires often contain significant fluctuation intensities down to 1 ms, or 1 kHz in frequency space. Measurements of instantaneous temperature and soot concentrations are important, because it has been shown that the time-averaged radiant heat flux from pool fires cannot be predicted from knowledge of the time-

averaged temperature and soot concentrations, due to the strongly nonlinear Planck radiation term (Fischer et al., 1987; Choi et al., 1994).

Heat Flux Gauges

With its interest in the heat transfer characteristics of large fires, Sandia has invested substantial effort to the development of rugged, inexpensive, and relatively accurate heat flux gauges and calorimeters for use in fires. Calorimeters are relatively large, typically cylindrical objects with well-known thermal and radiative properties, whose rate of temperature rise during a fire can be used with an inverse heat conduction model to determine the total net heat flux at that location within the fire (e.g., Gregory et al., 1989). Unfortunately, the large size and thermal inertia of calorimeters limits their spatial and temporal resolution of the heat flux. Faster, local heat flux gauges have been developed that can be used simultaneously at multiple locations within fires. Thin-plate "equilibrium" sensors use a large-diameter, thermally isolated sensor surface with a thermocouple attached to the interior side. This type of heat flux gauge is simple, economical, and robust, but is limited by its relatively long time constant, on the order of 10's of seconds (Gritz et al., 1995; Gritz et al., 1996). "Active" heat flux gauges depend on maintaining the gauge at a relatively constant, low temperature. Three types of active gauges have been applied in large fires: circular foil (Gardon) gauges, thermopiles (Schmidt-Boelter gauges), and transpiration radiometers. These gauges have significantly better time response than equilibrium-type gauges, down to tenths of a second, but are more costly and difficult to operate. The circular foil gauges and thermopiles are susceptible to condensation of fuel or water vapor onto the gauge surface, unless purge flow is provided, and all of the active gauges preferentially weight radiative heat transfer over convection (Gritz et al., 1995).

Bi-Directional Velocity Probe

Local velocity measurements in fires are important, in concert with temperature measurements, for the calculation of the convective heat transfer rates to embedded objects. The velocity field within fires also controls the entrainment of air into the fire plume. Unfortunately, accurate measurement of these velocities is very difficult, due to the relatively low buoyant velocities in the flame and the rapid, strong fluctuations in local velocity direction and magnitude in large fires. A simple, robust methodology for performing velocity measurements has been developed by McCaffrey and Heskestad (1974) that utilizes a bi-directional measurement of the difference between static and dynamic pressures and applies the Bernoulli relation to interpret the results (Schneider and Kent, 1989). Calibration tests have shown this probe to be nearly insensitive to the angle of approach of the flow, up to 50° off-alignment (Kent and Schneider, 1987). The accuracy of the velocity measurement is limited by the estimation of the time-dependent gas density, a function of gas temperature and the molecular weight of the local gases. The local gas temperature is typically determined with a sheathed type-K thermocouple, with a slow time response and sensitivity to radiation errors. The molecular weight of the local gases in fires is typically assumed to be that of air. The physical size of these probes, typically 2" (5 cm) from end-to-end of the open tubes and 1" (2.5 cm) tube diameter, constrains the spatial resolution of this measurement.

Spectral Emission

A few limited investigations of spectral band emission from fires have been conducted, primarily from small-scale experiments. The motivation for spectral band information is to gain improved knowledge of and confidence in the approximately graybody radiant distribution from soot within

fires, to assess contributions of gas-band emission to the radiant emission from fires, and to learn more about the turbulent mixing process within fires via time-resolved measurements of gas species concentrations. Relatively narrow-band emission measurements have often been performed in the near-infrared region, especially from 800-1000 nm, as a means of deriving soot temperatures through 2-color pyrometry, as will be discussed in the next section. In addition, Sivathanu and Gore (1991) have measured emission intensities at 4.0 and 4.5 μm with bandpass filters in front of PbSe detectors, in order to deduce the mid-IR broadband radiation intensity and the CO_2 emission intensity in turbulent acetylene/air flames. Choi et al. (1994) extended the CO_2 emission measurement to probes within a 10-cm diameter heptane pool fire. Recently, a fast-scanning infrared spectrometer has been utilized at Sandia to investigate the radiant emission from both small and large pool fires.

Soot Absorption/Emission Probe

The measurement of soot concentration (i.e., volume fraction) via light absorption and the measurement of soot temperature via 2-color pyrometry have been widely performed in laboratory flames and small fires. Sandia incorporated this technique into a water-cooled, insulated probe assembly that permitted measurements to be performed in large, open pool fires (Gritz et al., 1998a). This technique requires fairly obtrusive water-cooled probes to be used in large fire environments, most likely affecting some of the fire fluid mechanics and mixing in the vicinity of the probe. The spatial resolution of the measurement can be good, if a sufficiently sensitive detection system is used, but the probe volume is bounded by metal tube light pipes with a light purge gas flow, introducing an unknown, time-varying extent of flame quench at the ends of the tubes. The temporal resolution of this technique, as traditionally implemented, has been limited by the time constant on the lock-in amplifier used in conjunction with a chopper wheel that modulates the light source, usually resulting in 2 ms resolution. The primary difficulty in quantifying the soot volume fraction and temperature data provided by this technique is the need to assume suitable, wavelength-dependent optical properties (specifically, the extinction coefficient) of the soot being sampled. Measurements of the extinction coefficient of soot in a variety of flame and smoke plume environments have yielded values with over 2-fold variation, and no clear reason for this wide disparity is apparent at this time.

Soot TEM Sampler

Transmission electron microscope (TEM) grid sampling and analysis for soot particle microstructure has been applied both within the actively combusting portions of large pool fires (Williams and Gritz, 1998) and in the smoke plume above large fires (Radke et al., 1990; Mulholland et al., 1996). These measurements give useful information about soot primary particle size and extent of primary particle aggregation, reflecting the soot production and oxidation history of the particles and providing important information for calculating the optical properties of the soot aerosol. When high-resolution TEM (HRTEM) is performed, information about the nanostructural ordering of the soot is revealed. Unfortunately, any given TEM grid sample represents a snapshot in space and time in a large fire, such that the information provided by this analysis is primarily qualitative in nature.

Gas Sampling

In addition to the spectral emission measurements discussed previously for path-integrated CO_2 measurements, in a few cases water-cooled suction probes have been utilized to measure the time-

averaged concentrations of the major stable gas species at a given location within a fire. These investigations have typically utilized standard continuous emission monitor (CEM) gas analyzers for CO, CO₂, O₂, and total hydrocarbons (e.g., Bouhafid et al., 1988). The enclosure fire research program at the National Institute of Standards and Technology (NIST) has commonly used extraction probes to measure the major, stable gas concentrations as well as to determine the local stoichiometry of gases (Babrauskas et al., 1994; Pitts, 1995). With the extensive gas handling tubing needed for these measurements, as well as the use of a water knockout before the detectors and the inherent time response of the detectors themselves, the time response of these types of systems is generally no better than 30-40 seconds, even when the CEMs can be located in close proximity to the fire. For large, open pool fire environments, the response time would be worse, due to the need to locate the instruments a suitable distance away from the fire.

PIV and PLIF

Sandia has developed a unique capability for obtaining time-resolved, 1-m by 1-m simultaneous, spatially resolved images of particle image velocimetry (PIV) and planar laser-induced fluorescence (PLIF) for buoyant flows within the FLAME facility in Albuquerque (Tieszen et al., 1998). This technique has yielded quantitative 2-D flowfield information within the buoyant jet and the near-field entrainment zone for 1-m diameter flows and has also yielded qualitative information on fuel concentrations, using acetone PLIF as a fuel marker, and on PAH concentrations (using the broadband fluorescence signal). Unfortunately, these techniques are limited to non-reacting flows or lightly sooting flames, due to the rapid attenuation of the uv laser excitation and scattered light by soot.

Important Issues Involving Chemical Species in Fires

As can be seen in the preceding list of established diagnostics for fires, very little temporally and spatially resolved chemical species information has been collected in fires, the exceptions being the semi-quantitative CO₂ emission data that has been obtained in small fires. As a consequence, several important, unresolved issues still exist concerning the major chemical species concentrations in large fires. This information is required in the active flame region of large fires in order to assess the validity of common, simplified chemical assumptions (e.g., local chemical equilibrium) for tracking fuel consumption rates. Also, recent observations and measurements in large pool fires demonstrate that an interior "vapor dome" region persists for a considerable distance above the center of the pool, with significantly reduced temperatures, heat fluxes, and turbulent motion in this region (Gritzo et al., 1998b). Chemical characterization of this region is necessary to properly model radiative feedback to the pool or to engulfed objects. Radiative feedback to the fuel surface determines the local flux of vaporized fuel, affecting the burn rate, duration, and geometry of the fire. A chemical understanding of this interior region is also sought in order to develop and validate turbulence mixing models that describe the transport of entrained air into the interior of the fire. Furthermore, in all regions of large fires, the simultaneous measurement of soot concentrations and chemical species (particularly molecular oxygen and acetylene) is necessary to guide the application and modification of existing submodels of soot formation and oxidation. These submodels are critical to accurate prediction of the radiant heat flux within, and hence the hazard posed by, large fires. The purpose of this project has been to develop a technique for making these important measurements of gas species and soot in a number of different fire environments, in particular within large pool fires.

Options for Rapid Species/Soot Diagnostics

The objective for this diagnostic development is to perform measurements over a probe volume that is a few cm in dimension and with a temporal resolution of ≤ 0.01 seconds (i.e., ≥ 100 Hz). This physical dimension and timescale roughly correspond to the current limits in performing large fire simulations with available parallel-processing supercomputers. There are several potential techniques for performing the desired measurements of soot and major gas species concentrations. The techniques described below were considered before deciding that the combination of near-IR TDLs and a modified version of the traditional soot absorption/emission measurement was the best option for meeting the needs of this project.

FTIR Absorption Spectroscopy

The Fourier Transform Infrared (FTIR) absorption technique is widely used for identification and quantification of major and occasionally minor gas species in a variety of flows, especially in conjunction with the use of an extractive sampling line. This technique utilizes a broadband light source, roughly collimated as a beam, to illuminate the gas sample of interest. The transmitted light passes through a scanning spectrometer before being recorded on an IR detector. A spectral scan is processed via a Fourier transform to yield the spectrally resolved transmission spectrum, from which individual rotational-vibrational transitions corresponding to a given gas species may be quantified. The strength of the FTIR technique lies in its ability to perform wide wavelength scans, thereby measuring the concentrations of a number of gas species simultaneously and with a single instrument. However, the FTIR approach has a number of serious disadvantages for the current application. For example, the spectral resolution of the technique is determined by the size and precise motion of the spectrometer components, and therefore is usually limited for fieldable FTIR systems (to the order of 0.3 cm^{-1}), resulting in weaker detected linestrengths and significantly enhanced interference from water and CO_2 lines, which are ubiquitous in the infrared, especially at high temperatures. Furthermore, FTIR systems have limited temporal response (typ. 1-30s), depending on the desired spectral resolution and scanning range, due to the need to physically scan the spectrometer. Finally, FTIR relies on direct light absorption to perform its measurement, and thus is not sensitive to the weak overtone and combination band rotational-vibrational transitions in the near-infrared region. For many practical applications, including this fire application, techniques that can utilize standard, highly transmissive fiber optic cables are strongly desirable. The available fibers with good transmissive properties only extend through the near-IR (to $\sim 2\text{ }\mu\text{m}$).

Tunable Diode Laser Absorption Spectroscopy

Tunable diode laser absorption spectroscopy (TDLAS) utilizes narrow linewidth (typ. 0.001 cm^{-1}) diode lasers whose output is scanned across a spectral region containing one or more absorption lines of interest. The laser devices themselves are very small (on the order of a cm) and composed of solid-state semiconductors, making them suitable for field applications. The wavelength tuning of these lasers is performed by varying their temperature or electronically, by varying the injection current strength, and can thus be performed at very high rates ($> 10\text{ MHz}$). As a consequence, very fast measurements of gas species can be performed with TDLs. Furthermore, the use of electronic tuning allows for high-frequency wavelength modulation spectroscopy (wms), whereby a high-frequency sinusoidal dither is introduced to the spectral scan and detection is via a lock-in detector, yielding absorbance sensitivities on the order of 10^{-5} - 10^{-6} . The use of a coherent laser beam as the light source in TDLAS systems also has some practical advantages for transporting

and focusing the light, most clearly manifested in the commercial availability of fiber-coupled ("pigtailed") diode lasers in the near-infrared region. A photograph of a pigtailed, butterfly pin, near-IR distributed feedback (DFB) diode laser is shown in Fig. 1. The primary disadvantages of TDLs relate to their narrow tuning range ($\sim 15 \text{ cm}^{-1}$, or 4 nm, in the near-IR). In general, a given TDL can only be effectively used to measure a single gas species, and care must be taken in choosing TDLs for optimal detectivity of a gas species at different temperatures, due to the shift in peak transitions with temperature. Furthermore, TDLs are not always available at the desired wavelengths to make a particular species measurement. Overall, though, TDLs are much better suited than FTIRs to perform the desired temporally resolved measurements, especially in a non-laboratory environment.

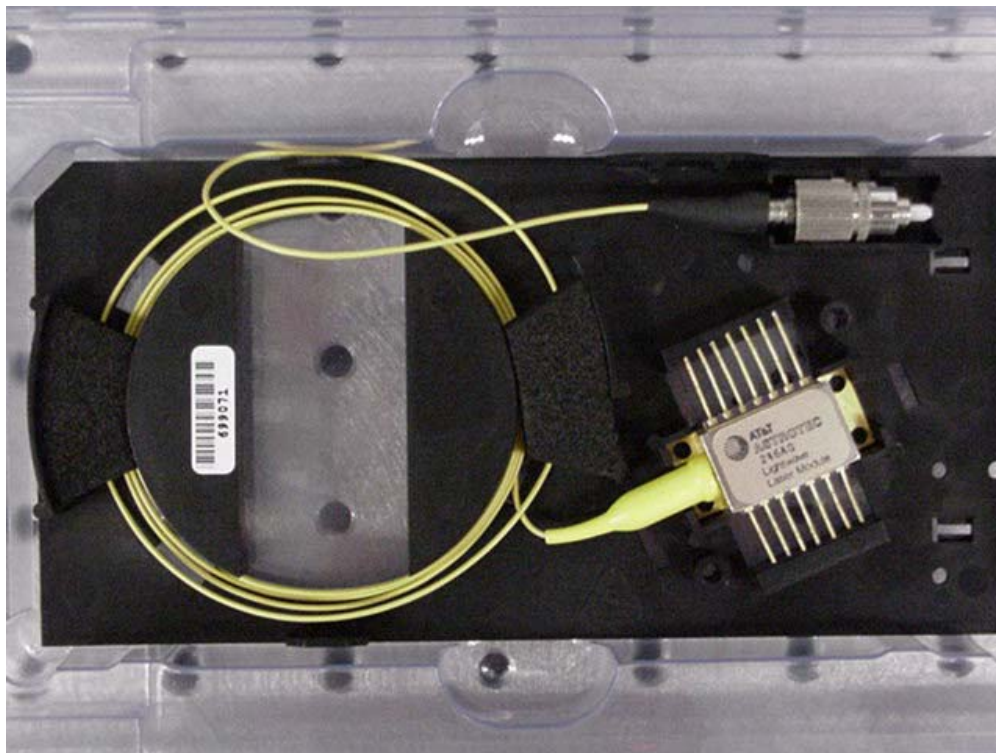


Figure 1. Photograph of a typical butterfly pin, near-IR DFB diode laser with a pigtailed single-mode fiber connection, as is typically used for gas species measurements with TDL. The 1-inch hole spacing on the underlying laser table gives a length scale. The large connection on the fiber end of the laser is the optical isolator, which minimizes backscatter feedback to the laser. The butterfly pins provide the electronic connections for operation of the laser and its associated thermoelectric cooler (many of the pins are not actually used).

TDL measurements of gas species have traditionally been performed in two general spectral regions: near-IR and mid-IR. A near-IR TDLAS system has many significant advantages over a mid-IR system, especially for field applications. Near-IR diode lasers are commercially mass-produced for the telecommunications market, assuring good quality devices with strong laser output (on the order of 5 mW) at well-characterized center wavelengths. As mentioned previously, for application to fiber-optic systems, near-IR TDLs can be purchased with an optical isolator and fiber-optic pigtail directly attached. The near-IR lasers are designed to operate at room temperature and are packaged within thermoelectric coolers (TECs) to control their lasing

wavelength. Similarly, sensitive near-IR detectors operate at room temperature. Conversely, mid-IR (lead-salt) TDLs require cryogenic cooling and are essentially custom-fabricated devices, frequently exhibiting multimode operation or dramatic changes in their operation over time, with very low power output (at best, 100's of μW). Flexible and efficient optical fibers are not available for mid-IR beam transport as required for the current field application. Mid-IR detectors also require active cooling. However, the use of mid-IR TDLs has two primary advantages relative to near-IR TDLs. First, the fundamental rotational-vibrational transitions of many molecules exist in the mid-IR, and these have absorption linestrengths that are typically orders of magnitude stronger than the overtone and combination band transitions in the near-IR. Second, the penetration of mid-IR light through particle-containing gas is generally much improved over shorter wavelength light, particularly if the particles in question are strongly absorbing (such as soot) or have a characteristic size on the order of a micron or less (again, such as soot). Thus, in some practical applications a mid-IR TDL system is preferable over a near-IR system. For the fire application, coupling of the laser light into a water-cooled probe is essential in order to perform the measurement and to provide sufficient spatial resolution, with the laser and all associated hardware thermally protected from the fire and ideally located in an instrument trailer some distance from the actual fire location. This situation gives strong motivation for using near-IR TDLs with direct fiber coupling, which was the approach chosen for this project.

LII versus 3-Line Soot Measurements

Soot concentration and temperature measurements have traditionally been performed using visible laser light absorption in combination with two-color emission pyrometry. The light absorption may be directly used to determine the soot concentration over the absorption pathlength by applying the Bouguer Law:

$$I/I_0 = \exp\left(-K_e \frac{f_v}{\lambda} l\right)$$

where I/I_0 is the ratio of transmitted to incident light, K_e is the extinction coefficient, f_v is the soot volume fraction, λ is the optical wavelength, and l is the optical pathlength through the absorbing soot.

The extinction coefficient that is used in this expression could either be measured directly in a calibration soot flow (Mulholland and Choi, 1998; Zhu et al., 2000) or can be calculated by assuming that the soot shows Rayleigh-limit (i.e. small-particle) behavior and that a previously measured index of refraction for soot is appropriate for the soot in the present application. Having determined the soot concentration over the absorption pathlength, the equation for two-color emission pyrometry can be solved to yield the soot temperature over the absorption/emission volume. This approach has been referred to as the 3-line soot technique and has been widely applied to laboratory studies of sooty fires, with the HeNe laser (632.8 nm) the de facto standard for this measurement, due to its ready availability and relatively long wavelength (which tends to put the soot in the Rayleigh limit).

An alternative to laser light absorption measurements for soot concentration has recently been developed. This technique is known as laser-induced incandescence (LII), and utilizes a pulsed, high-energy laser to heat the soot up to its vaporization point (at 4000 K) and then detects the thermal emission from the heated soot. This technique offers advantages over the laser light absorption method in terms of sensitivity and in its ability to perform instantaneous line or planar

images of the soot concentration. In general, this technique needs to be calibrated against another means of measuring soot concentrations (most often laser extinction) and therefore suffers from similar uncertainties over absolute accuracy as these other techniques. Furthermore, for application to turbulent or strongly sooting flames, this technique is inferior to laser light extinction in overall accuracy because of the extinction of the LII signal from its location of origin to the imaging detector (signal trapping) and because of the effect of extinction of the laser beam as it traverses the probe volume. For these reasons, the 3-line soot technique has been adopted as the best available means of measuring soot concentrations and temperatures using a water-cooled probe in large pool fires.

TDL/Fire Diagnostic Development

The successful application of tunable diode lasers for species measurements in a fire environment has involved a number of important technical developments, which may be grouped according to the following considerations: assessment of the best detectable gas species to measure in fires and the optimal spectral locations for their measurement, development of a suitable laser multiplexing approach, and design of a suitable technique to optically multipass the laser beam through the probe volume, thereby improving the inherent sensitivity of the measurement.

Selection of Gas Species

Based on past experience with TDLs and an understanding of the fire program data requirements, an initial suite of molecules to be detected in the fires was proposed, including methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), and water (H_2O). Molecular oxygen (O_2) was recognized as an important species to track the air entrainment and mixing within the fire, but the likelihood of success of measuring this species together with the other suggested species was unknown, based on the spectral location of the strongest accessible oxygen transitions (at $\sim 0.76 \mu\text{m}$; a classically forbidden electronic transition band), which is significantly different from the $1.3\text{--}1.7 \mu\text{m}$ range of near-infrared rotational-vibrational transitions for the other target species. Convenient beam combining, transmitting, and separating components are not readily available for such disparate wavelengths. Acetylene (C_2H_2) has long been proposed as the key fuel pyrolysis species responsible for soot particle nucleation and surface growth, so its measurement would provide important information about soot formation chemistry within fires. Unfortunately, little TDL work had been performed with acetylene before this project, with no information in the literature about its detectability at high temperatures. Hydroxyl radical concentrations (OH) are also of interest for flame structure and soot oxidation reasons, but little work has been performed measuring high temperature OH with TDLs.

Expected species concentrations

In addition to these general considerations, determination of the most promising target species involved analysis of the likely range of concentrations of these species in aviation fuel fires. A literature search revealed the best available experimental information on the flame chemistry of aviation fuels is the work over the past decade at the CNRS combustion lab at Orléans, France. This group has investigated the oxidation of kerosene and of decane using a jet-stirred reactor operating at pressures ranging from 1 to 40 atm (Guéret et al., 1990; Balés-Guéret et al., 1992; Dagaut et al., 1994a and 1994b) for a range of mixture stoichiometries at intermediate temperatures ($\sim 1000 \text{ K}$). CNRS has also performed detailed gas chromatography (gc) analysis of the flame structure of fuel-rich, premixed kerosene and decane flat flames, at both low pressure

(Delfau, 1990) and at 1 atm (Douté, 1995). This latter investigation is believed to be of most direct relevance for the expected predominate local chemical structure in pool fires, a wrinkled laminar diffusion flamesheet (at 1 atm). All aviation fuels are essentially minor variants of common kerosene, so no major differences in the concentrations of the primary combustion intermediates are expected for the actual JP-8 fuel chemistry and that for kerosene. The atmospheric-pressure, kerosene premixed flame that was investigated by CNRS at an equivalence ratio of 1.7 shows peak concentrations of CO, H₂, C₂H₄, C₂H₂, CH₄, and C₂H₆ of 17, 9, 2.2, 1.7, 1.3, and 0.3 mole-%, respectively. Kerosene has a nominal chemical composition of C₁₁H₂₂, so the expected product concentrations at the flame sheet of a diffusion flame of kerosene in air are 13 mole-% each of water and CO₂. These peak concentration values give some sense of the relative ease of detection that is expected for these different species, when convoluted with the actual available detection linestrengths that are available. However, in themselves these estimations are inherently imprecise because the TDL measurement technique is integrating across a few cms of sample volume, thereby integrating across the entire mixture fraction space of one or more flamesheets at any given instant, in addition to unknown volumes of pure fuel, pure air, or pure products. A more precise analysis of the ease of detection of the different chemical species would incorporate a full mixture fraction integration of chemical concentrations, convoluted with a mixing model, but this was not pursued in this project.

Linestrength predictions

Actual specification of a desired TDL for making a species measurement also involved knowledge of the available sources and wavelengths for diode lasers and analysis of the strongest transition linestrengths at high temperatures. The HiTran spectral database (Rothman et al., 1998) and the companion HiTemp database for CO₂ and H₂O, initially developed by the USAF for interpretation of atmospheric measurements, are the standard sources of predictions for small molecular absorption locations and linestrengths, but they have weak coverage at near-IR wavelengths and are known to be unreliable for predictions at elevated temperatures. As part of this project, the HiTran and HiTemp databases, as well as supplementary literature sources, have been extensively investigated, in order to identify the spectral locations and linestrengths of the proposed target molecules. This survey revealed that little was known about the high temperature absorption spectra of several of the candidate species in the near-IR, particularly water and carbon dioxide, which are also the dominant interfering species in combustion environments because of their numerous transitions. Figure 2 shows the room-temperature transition linestrengths of selected gas molecules in the near-IR region that is nominally covered by easily obtainable diode laser sources (1.3-1.7 μm). These linestrength values are generally expected to be valid within 10% uncertainty, except that some transitions of H₂O are undoubtedly neglected. Fig. 3 shows estimated linestrengths at elevated temperature for these same molecules (except for methane). The high-temperature CO, CO₂, and H₂O linestrengths are those predicted by HiTran and HiTemp, whereas the high-temperature acetylene linestrengths are those predicted by calculating the partition function for acetylene when using the Born-Oppenheimer approximation, rigid-rotor model, and simple harmonic oscillator model, as has been shown by Nagali et al. (1996) to give accurate predictions for methane. The primary features to note in comparing Figs. 2 and 3 are the weaker transition strengths at high temperatures, especially for CO₂ and C₂H₂, the broadening of the water transition envelope to longer wavelengths (smaller wavenumbers), and the shifts in the peak transitions of the various species.

In addition to the general trends noted above with high temperatures, the HiTemp database predicts the existence of fairly strong hot-band CO₂ transitions from 6409-6807 cm⁻¹ (1.47-1.56 μm). The existence of these transitions might pose an opportunity for improved detection of CO₂, but also

would undoubtedly contribute to spectral interference in measuring a number of other species in this spectral range. As a consequence of the uncertainty in the high-temperature transition strengths, significant effort was expended in this project attempting to measure the high-temperature spectra of the candidate species and evaluating potential interferences from water and carbon dioxide transitions. Two separate experimental facilities were used for these investigations. First, an existing low-pressure, flat-flame FTIR facility was utilized. This facility had the advantage of allowing, in theory, the probing of chemical species from the fuel-rich upstream side of a premixed flame zone, through the flame zone, and downstream of the flame zone, with full spectral access of the near-infrared region with the use of appropriate optics on the Bomem high-

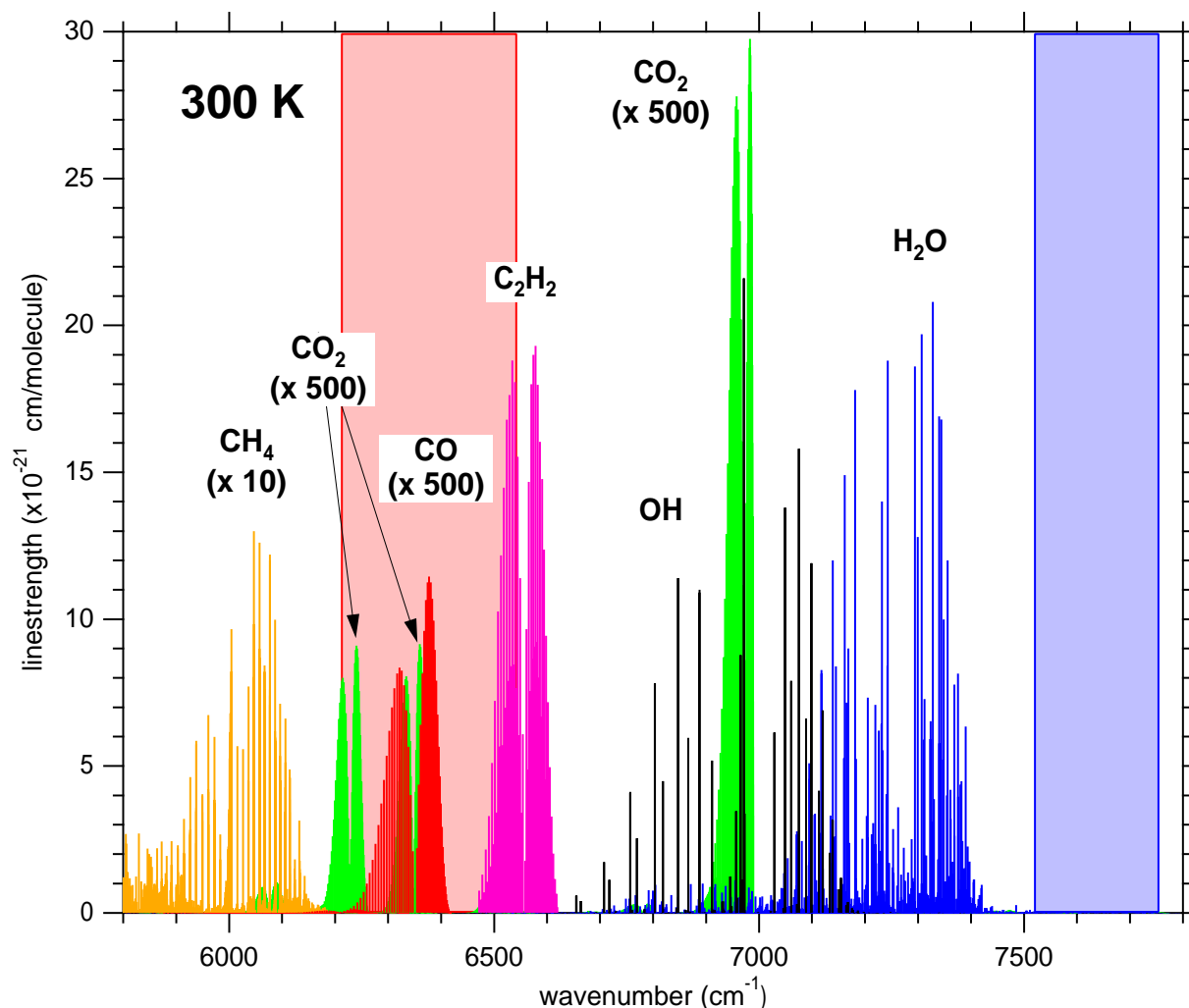


Figure 2. Room-temperature HiTran database linestrengths of near-IR transitions of gas species of potential interest, combined with acetylene FTIR measurements (acetylene is not included in the HiTran library). Note the scaling of the transitions of methane, carbon monoxide, and carbon dioxide. The blue shaded region ($7520\text{--}7750\text{ cm}^{-1}$) represents the commercially available diode wavelengths centering on the $1.31\text{ }\mu\text{m}$ band. The red shaded region ($6210\text{--}6540\text{ cm}^{-1}$) gives the current commercially available International Telecommunication Union (ITU) grid lasers, centering around $1.55\text{ }\mu\text{m}$.

resolution FTIR. Unfortunately, the sensitivity of FTIR systems for transmission measurements is relatively poor, and the very weak molecular transitions being probed in the near-infrared proved to be very difficult to measure. To increase the system sensitivity, multipass mirror optics were installed in the side-arms of the probed burner cube, allowing 20 passes of the FTIR beam through the flame gases before detection. Multipassing of the large FTIR beam resulted in a physical probe volume in the flat flame that was several cm in height, reducing the net benefit of multipassing for the spatially confined reactive species in the flame. In addition, diffusion of species into the dead volume regions in front of the multipass mirrors introduced uncertainties in the effective pathlength being probed and in the temperature uniformity of the probed species. In all, spectra were recorded for methane and acetylene at relatively low temperatures, right at the burner lip, and for CO₂ and H₂O at relatively high temperatures. CO spectra could not be detected in this facility, but knowledge of the high-temperature spectra of CO is well known, such that new experimental measurements are not required.

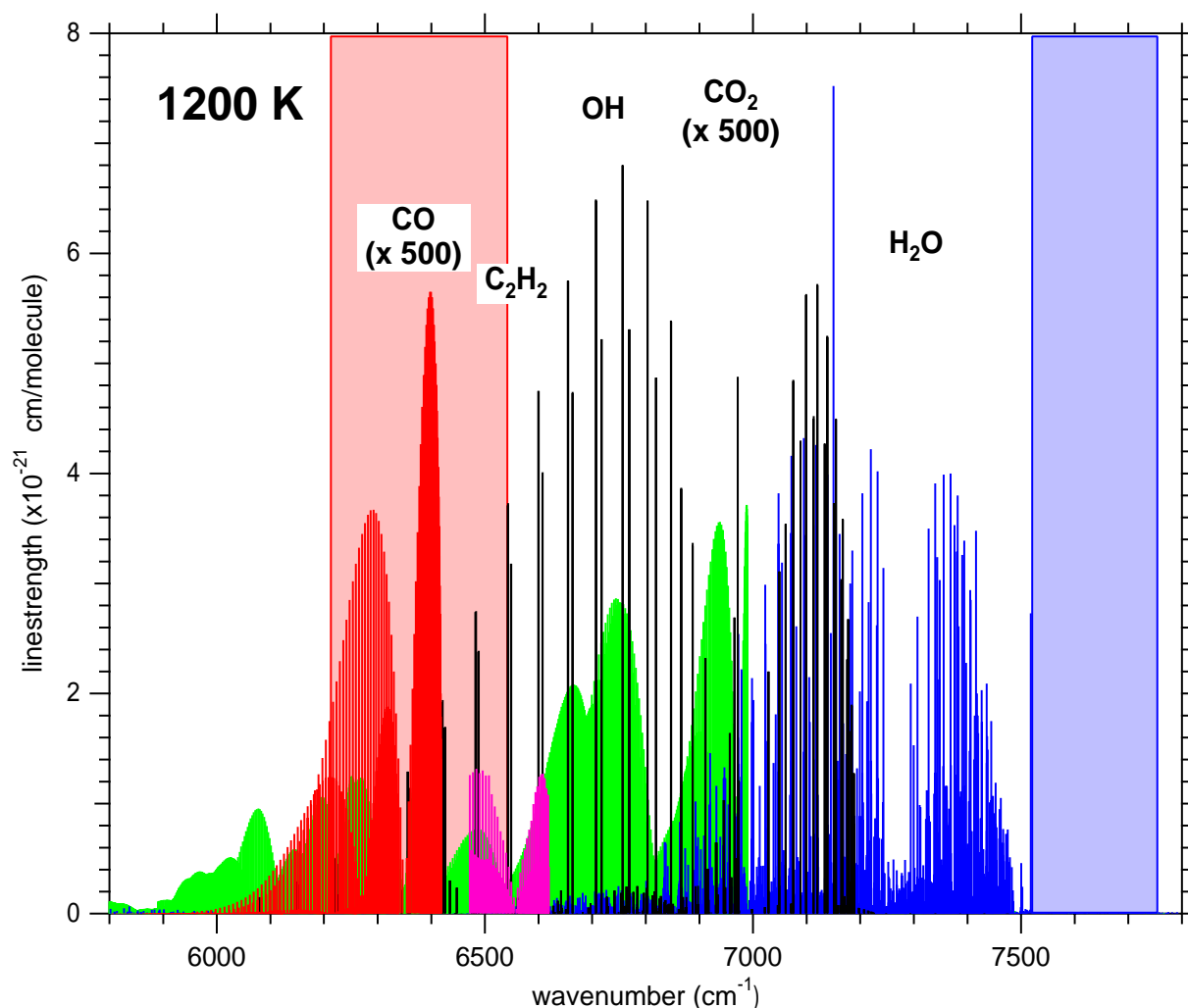


Figure 3. High-temperature HiTran and HiTemp database linestrengths of near-IR transitions of gas species of potential interest, combined with acetylene FTIR measurements with partition function corrections for elevated temperature.

In order to improve the spatial and thermal uniformity of the probed gas environment, a laminar-flow, combustion-driven optical furnace was utilized. With this facility, widely tunable external-cavity TDLs were used to record the absorption spectra, together with a combined balanced-ratiometric detection (BRD) and wavelength modulation spectroscopy approach to improve system sensitivity. External-cavity TDLs often contain mode hops and cannot be modulated at high frequencies, reducing their utility for sensor or field measurement applications, but their relatively wide tuning range (~ 100 nm) makes them very useful for conducting spectral surveys. (The distributed feedback tunable diode lasers that are best suited for high-fidelity measurement and sensor applications have a tuning range of ~ 4 nm, in comparison.) Our work in the optical furnace focused on determining whether relatively strong, high-temperature CO_2 transitions (hot-bands) postulated in the HiTemp database, but not experimentally verified, really existed, and in measuring the interfering water transitions through the spectral regions appropriate for measuring carbon monoxide, methane, and acetylene. A photograph of the optical setup for these measurements is shown as Fig. 4. Our measurements demonstrated that the postulated strong CO_2 hot-bands did not exist, in agreement with the inferences from a few other recent studies. In addition, although we measured many more high-temperature water transitions than are contained in the existing spectral databases, suitable interference-free high-temperature transitions were identified for CO, methane, and acetylene.

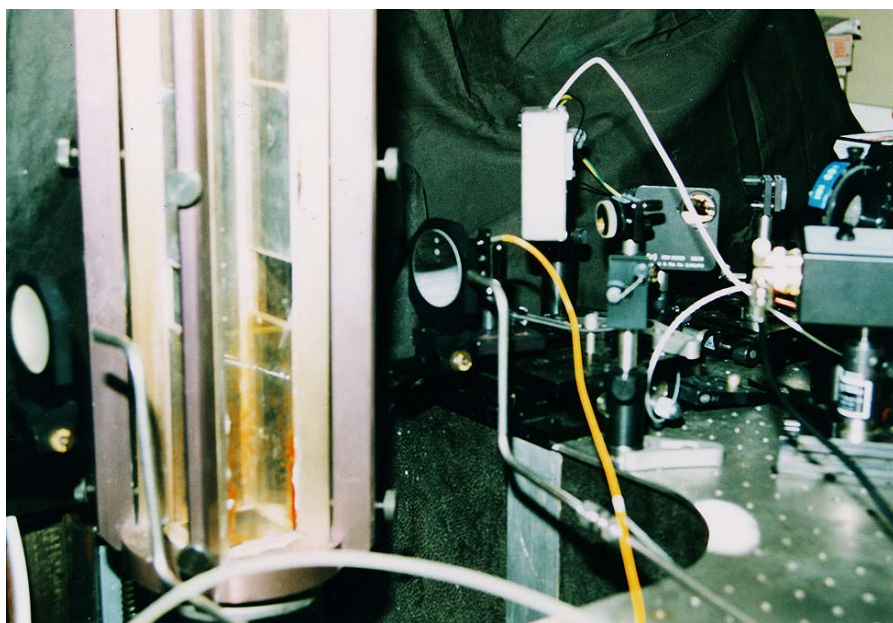


Figure 4. Photograph of the optical setup for performing tunable diode laser measurements of absorption spectra at high temperatures in the near infrared. The transparent, quartz-walled furnace is fed by the products of a diffusion flamelet-based flat flame (Hencken burner), which can provide gas flows with a variety of oxidative product concentrations and temperatures.

The very weak, second-overtone transitions of CO_2 that are known to exist at high temperatures would be very difficult to detect in flames, and the planned measurement of water concentrations should give appropriate information on combustion product concentrations (to the extent ambient air is relatively dry). Therefore, CO_2 was dropped from the target list of molecules. Measurements of O_2 are possible using TDL systems probing the classically forbidden A-band

electronic transitions near 760 nm. However, 760 nm diode lasers are not currently available (they used to be manufactured by Mitsubishi), and the oxygen transition wavelength requires the use of a different type of detector than the InGaAs detector that works best over the 1.3-1.65 μm wavelength range that contains the other species of interest. Therefore, this species was also dropped from the list of target species. Hydroxyl radical was also dropped as a candidate species, because of its low concentrations in the flame, particularly when spatially integrated across the probe volume, and because of the viewpoint that measurement of this would yield less information than that provided by the other candidate species. Acetylene was initially suggested as a possible candidate species, based on its importance in soot formation and growth chemistry, but tempered by lack of knowledge of its high-temperature spectra. Our measurements, combined with calculations of the partition function for acetylene, suggest that it has relatively strong transitions at high temperatures, some which are free of water interferences. For these reasons, we chose to measure acetylene. The final list of target species for measurement in JP8 pool fires includes methane, acetylene, carbon monoxide, and water. Off-the-shelf DFB butterfly-pin lasers manufactured by Lucent Technologies were selected for detecting acetylene, carbon monoxide, and water vapor. The methane laser was a specialty order item that was acquired from NEL America.

Laser Multiplexing

As a consequence of the narrow tuning range of individual diode lasers (particularly the distributed feedback diode lasers best suited for the fire application), several lasers must be utilized for applications involving the detection of multiple gas species. Historically this has been achieved by using a separate optical path and detector for each laser. However, for system compactness and simultaneous detection over the same optical path, some means of combining the multi-wavelength light, or multiplexing, is desired, particularly for the probe-based fire measurements to be performed during this project. Recently, several groups employing TDL diagnostics for combustion-related measurements (Stanford Univ., PSI, and Southwest Sciences) have demonstrated techniques for multiplexing two (and, in one case, three) lasers. These techniques have varying degrees of applicability to the fire measurement problem, and all have difficulty in multiplexing as many as four or five lasers, as is desired here. In general, combining the laser light onto a single fiber-optic for launch across a probe volume is trivial, since communication-grade near-IR fiber-optic couplers are available that do not result in significant laser light loss or introduce significant optical étalons (a major source of noise in fiber-based measurement systems). The challenge in multiplexing TDLs is to deconvolve the different wavelengths (or their resulting detector signals) once the laser light has passed through the probe volume.

The simplest technique for multiplexing diode lasers is to use temporal staggering of the injection current ramp of each laser. This technique takes advantage of the fact that a minimum, threshold injection current is needed for diode lasers to produce light and that a current ramp may be used to scan distributed feedback TDLs across a given absorption feature. With suitably fast detection electronics, these ramps can be scanned at frequencies much higher (e.g., at 10 kHz) than the highest frequency of gas species concentration variation expected in the probe volume. Deconvolution of the multiplexed signal (i.e., temporal fragmentation) occurs during digital storage in a computer. For sensitive TDL measurements, high-frequency modulation of the injection current is typically imposed onto the scan ramp and the detector signal is demodulated at twice the modulation frequency (second-harmonic detection) with a phase-matched lock-in amplifier. To apply this time domain multiplexing technique to a system of lasers with high-frequency modulation, the modulation frequencies must have well-matched phases. Also, as the

number of multiplexed lasers increases, the overall sampling time associated with a scan of all the lasers increases and the temporal resolution of the measurement suffers.

A second technique for multiplexing TDLs is to physically separate the individual laser beams before each is detected on its own detector, for example, by diffracting the transmitted light off of a grating. For application to the probe-based measurement required in fires, this technique requires collection of the transmitted light onto a fiber-optic to transport the light out of the fire before separating the light. Collection of the transmitted beam onto a fiber can result in substantial optical losses, particularly since a small-diameter, single-mode fiber is probably needed in this case in order to have the grating/detectors assembly well-removed from the fire and still preserve the phase coherence of the high frequency modulation of the signals. Also, we are interested in detecting two hydrocarbon species (CH_4 and C_2H_2), whose transitions are very close to one another spectrally and may be difficult to resolve with a grating that also resolves the much wider spectral separations between these species (at $\sim 1.6 \mu\text{m}$) and water vapor (detected at $1.31 \mu\text{m}$).

The technique that was chosen for this project is referred to as frequency domain multiplexing, and consists of segregating the signals from the different laser sources through the use of laser modulation at separate, characteristic high frequencies. The principal advantage of this approach is the opportunity for rapid sampling of all laser signals, and therefore the most optimal temporal resolution. This technique requires the use of the same number of high-speed, low-noise, RF lock-in amplifiers as there are multiplexed lasers. Commercial RF lock-ins are expensive and do not have sufficient time response to allow the resolution of absorption structures in a 1 kHz ramped TDL scan (a time constant around $10 \mu\text{s}$ is needed, while the best available commercially gives a time constant of $100 \mu\text{s}$). However, custom-built lock-ins are used often for TDL measurements in the atmospheric sciences community and are reported to operate very well (e.g., Werle, 1998). Therefore, we contacted researchers in Sandia's RF electronics area and with their assistance specified the combination of filters, amplifiers, splitters, and mixers required to construct a dual RF lock-in system with a time response of $8 \mu\text{s}$. Schematic of the electronic components that comprise this TDL dual lock-in multiplexing system are shown as Figs. 5 and 6.

One significant concern in the application of this approach to multiplexing is the extent to which signals from one laser can be effectively masked from the lock-in signal of a different laser. In order to evaluate this effect, the relative modulation frequencies of two lasers were varied, and the lock-in response of a laser that was turned off was evaluated for bleed through from the other laser signal. The results are shown in Fig. 7, from which it is clear there is a small amount of bleed when the lasers are modulated at frequencies that are separated by 20 kHz, but essentially no bleed occurs for a modulation separation of 100 kHz.

In Situ Multipass Optics

Very small molecular absorption signals were anticipated and ultimately verified in the fire environment, because of the high temperatures, presence of light-attenuating soot, and the desired small probe volume of the measurement. High temperatures significantly reduce the ability of the TDLAS technique to detect gas species through the combined effects of gas density reduction and reduced molecular transition strengths (a consequence of increased partitioning of internal energy via the Boltzmann distribution). Sensitive measurements of species concentrations using near-IR TDLs are typically only achieved using long pathlengths, and, to a certain extent, long signal integration times. The rapid response ($> 100 \text{ Hz}$) and short measurement length (2–4 cm) desired for grid-level fire measurements demands that improvements be made in the sensitivity of the

TDL system under these constraints. One important means of improving the molecular sensitivity over a fixed probe volume is to multipass the laser beam through that volume before detecting the path-integrated absorbance. This is typically done by locating high-reflectivity spherical mirrors on either side of the probe volume and using established, stable reflectance patterns (e.g., the White, Herriott, or Lissajous patterns) of off-axis beams to conduct a known number of traversals before the beam exits the mirror enclosure.

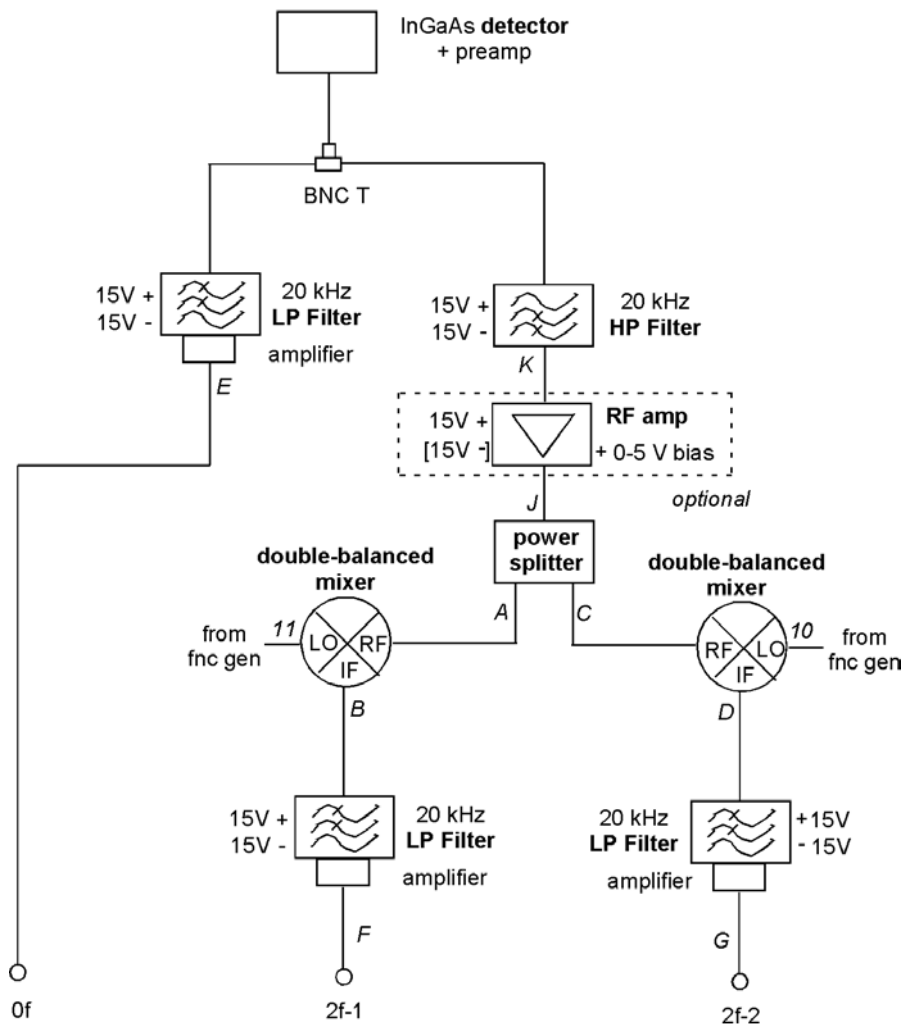


Figure 5. Schematic of the electronic components used to process a given near-IR detector output for both the base ramp waveform (the “0f”) and the second harmonic (“2f”) waveform for two multiplexed lasers.

Two complications of applying this technique for pool fire measurements are the required open geometry between the two parallel mirror surfaces and the effect of transient broadband attenuation of the laser light due to soot particles in the probe volume or due to beam steering within the probe volume. Typically, in order to assure good alignment between the parallel mirrors in a multipass measurement, the mirrors are rigidly attached to one another. This is not possible for a relatively

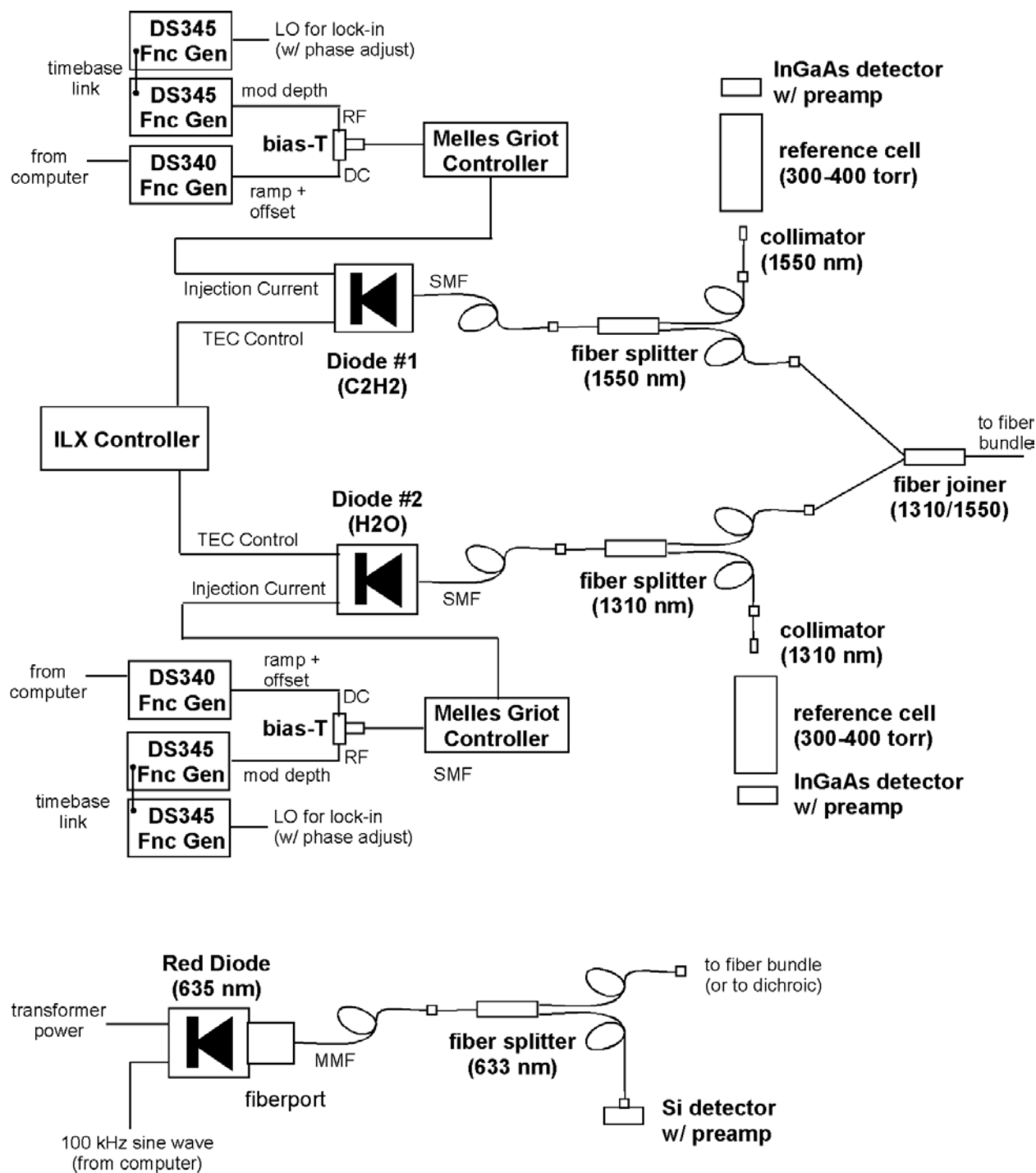


Figure 6. Schematic of the electronic components and fiber cables used to multiplex two near-IR TDLs, including reference cells. Also shown are the components of the laser end of the red diode system used for measuring soot concentrations.

non-perturbing water-cooled probe in fires, so instead, stable, fine-positioning mounts were tested and ultimately used for maintaining mirror alignment. Near-IR TDLs have become increasingly valuable tools for performing gas species concentration measurements of utility to atmospheric

science and chemistry. For this application, similar demands on measurement sensitivity and even more stringent demands on alignment stability are required, as such measurements are typically performed under aircraft wings, on board weather balloons, or even on rockets configured for atmospheric measurements. In all of these applications, TDLs have been successfully configured for multipassing using the Herriott cell design (Herriott et al., 1964; May, 1998). Based on this track record, we specified and tested a pair of Herriott cell mirrors in our laboratory that were 2 inches in diameter. A photograph of these 2-inch mirrors and the associated Herriott cell beam pattern is shown as Fig. 8. The performance of this Herriott cell system in a laboratory transient buoyant diffusion flame will be discussed later.

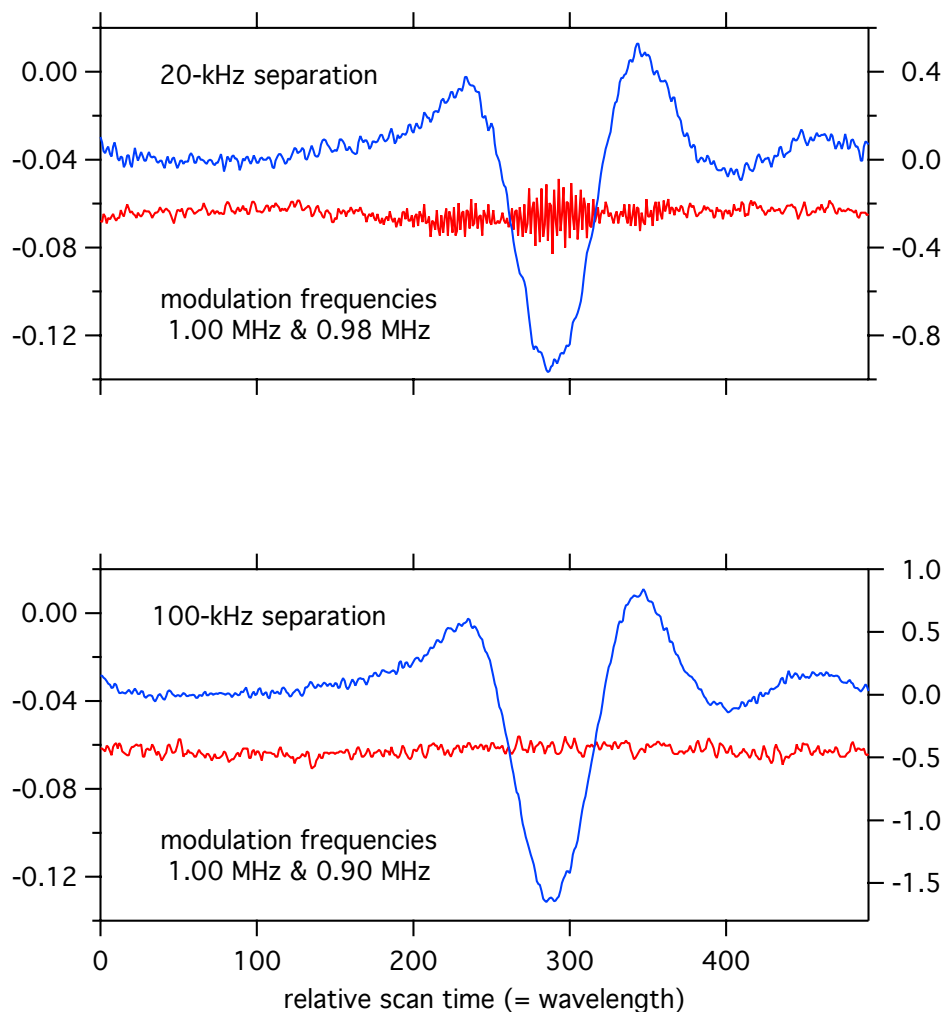


Figure 7. Plots showing the relative amount of leakage $2f$ signal, in red (left axis, in volts) for a given molecular $2f$ signal, in blue (right axis, in volts).

The presence of light-absorbing soot in the probe volume has implications for the optimal total pathlength of the laser in making the species measurements. The signal response of the TDL system is proportional to the product of the transmitted laser light intensity and the optical pathlength through the probe region. Since the transmittance is an inverse exponential function of broadband absorption, in the limit of a fixed background noise level the signal/noise ratio reaches a peak for a certain optical pathlength. For the soot volume fractions previously measured in a 6-m

JP-8 pool fire and for the TDL wavelengths of interest in this project, that optimal pathlength is, on average, $\sim 20\text{--}30$ cm. Therefore, for a desired 2–4 cm probe volume length, a 10-pass optical arrangement will probably work best. Of course, laser light losses from beam steering convolute this analysis, as they are not likely to follow any predetermined function as the number of optical passes increases.

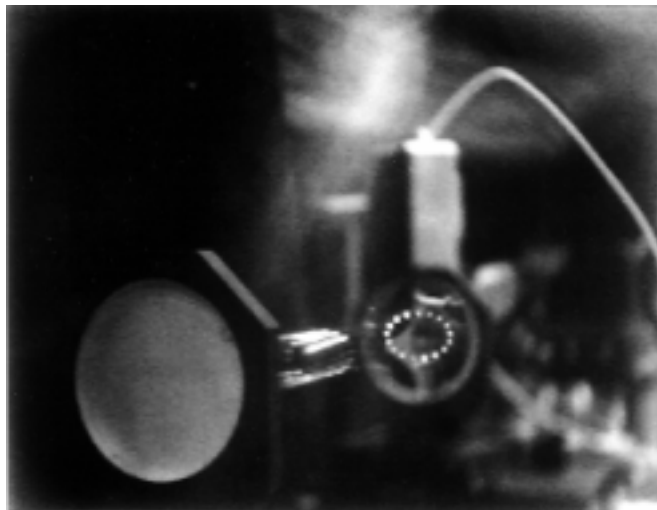


Figure 8. IR camera image of laser light scattering off of a Herriott cell mirror and off of liquid nitrogen vapor between the two mirrors constituting the cell.

Soot Diagnostic Development

The “3-Line” soot absorption/emission diagnostic technique was briefly described in the introduction of this report. As traditionally implemented, a HeNe laser is used for the laser absorption method, with a chopper and lock-in detector used to assure no influence of the natural thermal emission of the hot soot on the detected laser absorption. Bandpass filters, varying in spectral width from 10 to 100 nm, are typically used at wavelengths varying from 750 to 1000 nm in front of photomultiplier tubes. For this project, we were constrained to fitting the soot diagnostic within the spatial constraints of a Herriott cell mirror system for performing multipassing of the TDL laser beam. The most obvious way in which to do this was to utilize the center of the probe volume by drilling out the center of the Herriott cell mirrors, which are not utilized in a standard Herriott cell optical resonator. This spatial requirement places limitations on the optics used to project the absorption laser beam and to collect the emitted light for the pyrometry measurement, as centerline holes ≤ 1 cm in diameter were desired. To accommodate this, a new system for performing this measurement in fires was derived, complete with a re-evaluation of the best available laser light sources and detectors. This new system design is detailed below and presented schematically in Fig. 9.

Laser Sources

Light choppers have limited frequency bandwidth and take up physical space in the optical train. Consequently, an electronically modulated diode laser was chosen to perform this measurement.

In keeping with the traditional use of HeNe lasers for this measurement, a 5 mW 635 nm diode (from LaserMax Inc.) was used, that can be fully modulated at frequencies up to 3 MHz.

Optics

In order to fit the laser collimation and collection optics within the available space, standard multimode solid-core fiber with a diameter of 62.5 μm was used for conveying light to and from the probe volume. A fixed 7 mm aspherical collimator (from OFR – Optics for Research) was used to launch the red laser beam and a fiber coupler with an 8 mm aspherical lens (also from OFR) was used to recouple the laser light to a fiber for transfer out of the probe. The use of a single, solid core fiber eliminates concerns over the influence of beam steering on the results of previous applications of this technique in flames with fiber bundle light collection.

Detector Choices

Avalanche photodiode detectors (APDs) have been gaining in popularity over the past decade, due to their lower voltage requirements and enhanced linearity relative to photomultiplier tubes (PMTs). For the most sensitive visible light detection applications, PMTs are still preferable over APDs, but for this application it was expected that sufficient light would be present to allow the use of APDs for the pyrometry measurement. APDs are also smaller and generally more easily used in field applications than PMTs. Consequently, two small-area, high-gain, low-noise silicon APDs were acquired for this project to perform the soot pyrometry measurement.

Emission Wavelengths

The choice of emission wavelengths for the pyrometry measurement involves a number of competing compromises. First, the relative signal strength as a function of wavelength must be considered, which is a convolution of the increasing radiant intensity with increasing wavelength in the near-IR at soot emission temperatures and the decreasing sensitivity of silicon-based detectors for wavelengths longer than 850 nm. Also, increasing the spread of the two wavelengths increases the theoretical temperature resolution of the measurement, but comes at a cost of increased uncertainty over the variation in the extinction coefficient of the soot over the detected wavelength region. Similarly, increasing the bandwidth of the bandpass filters increases the signal to noise in most cases, but comes at a cost of decreasing temperature resolution. With all of these considerations, a decision was made to use wavelengths of nominally 850 nm and 1000 nm for detection of the soot emission, with filter bandwidths of 20 nm. Coupled with the Si APDs, these choices for spectral filters gave sufficient signal strengths in laboratory unsteady diffusion flames, especially those fueled by acetylene. A high-temperature blackbody source was used to check the calibration of the APD pyrometry system; the results are shown in Fig. 10. These measurements were performed without waiting for the blackbody to equilibrate at each documented temperature, and presumably the agreement with Plank's Law would be even better if more care had been taken in performing the measurements. Nonetheless, these measurements demonstrate that this pyrometry system can resolve a wide range of temperatures, from nearly 1000-1800 K, when the emitting medium is optically thick.

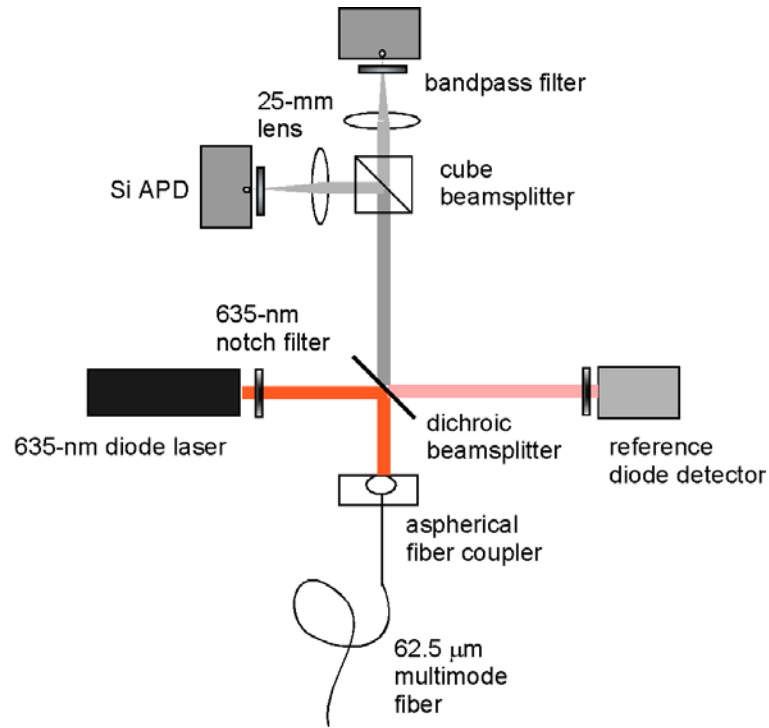


Figure 9. Schematic of the soot absorption/emission diagnostic system implemented for soot concentration and temperature measurements in concert with TDL measurements of gas species concentrations.

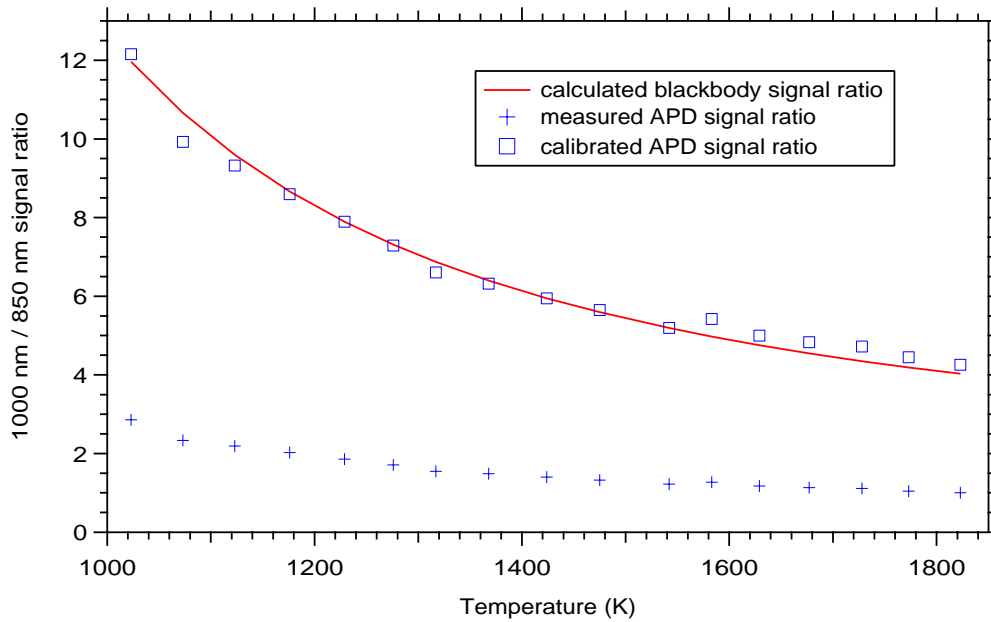


Figure 10. Results from a rapid calibration of the soot emission pyrometry diagnostic system, utilizing a high-temperature blackbody source.

Laboratory Development and Testing

With the proposed application of the novel technique for multipassing the TDL beam in a turbulent fire environment, laboratory testing was performed in buoyant, unsteady diffusion flames to evaluate the likely frequency response of the coupled flame/measurement system and to determine the effects of soot absorption and beam steering on TDL laser transmittance in the Herriott cell configuration. A chief concern was whether the transmitted laser light could be effectively recoupled into a single-mode or multimode fiber optic cable, so several combinations of light collection were investigated, including focusing directly onto an InGaAs detector element and coupling into fibers. In addition, the soot absorption diagnostic was evaluated for any influence of beam steering on its response. Most of the laboratory experiments were conducted with natural gas as the fuel. A photograph of the overall flame setup and a close-up of the active end of the Herriott cell setup are shown as Figs. 11 and 12. In order to evaluate beam steering effects directly, nitrogen was added to the natural gas until the flame turned blue, indicating that no soot formation was occurring in the flame. In the testing of the soot diagnostic, acetylene-fueled flames were also used. The principal results of these investigations are given below.

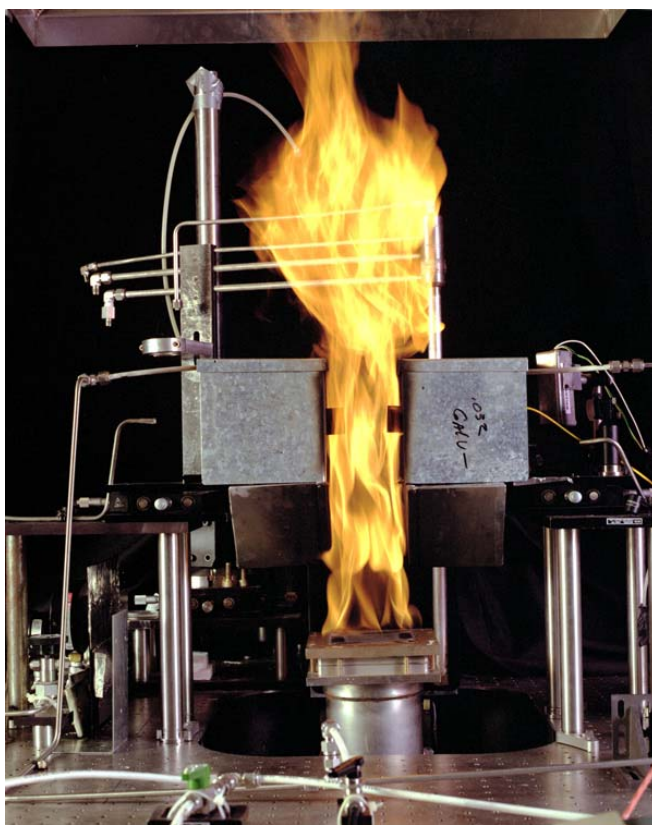


Figure 11. Photograph of an unsteady, buoyant diffusion flame of natural gas, with sight tubes and air-cooled housings for performing investigations of near-IR TDL multipassing in a fire-relevant flame environment.

Frequency Spectra

The power spectral density (PSD) functions for near-IR ($1.5\ \mu\text{m}$) measurements in a natural gas unsteady buoyant diffusion flame are shown in Fig. 13 for various combinations of light collection

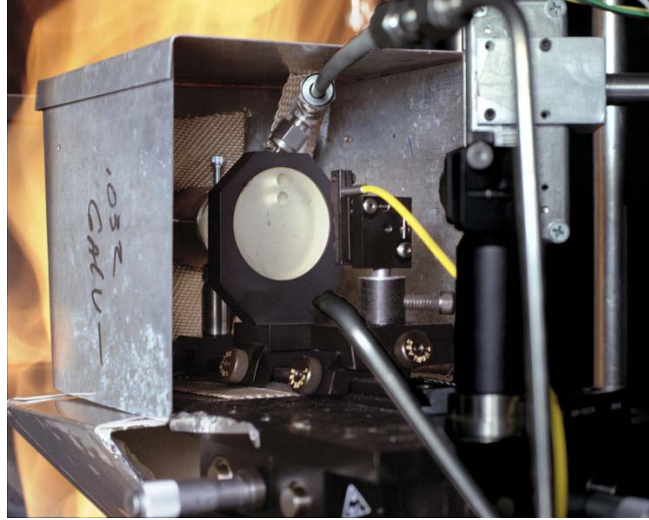


Figure 12. Photograph of the input/output end of the Herriott cell for laboratory investigations. The yellow single-mode fiber provides the laser light to a collimator that projects the laser into the Herriott cell. The beam exits the Herriott cell at a small angle from the incident beam and in this case is focused directly onto a photodetector.

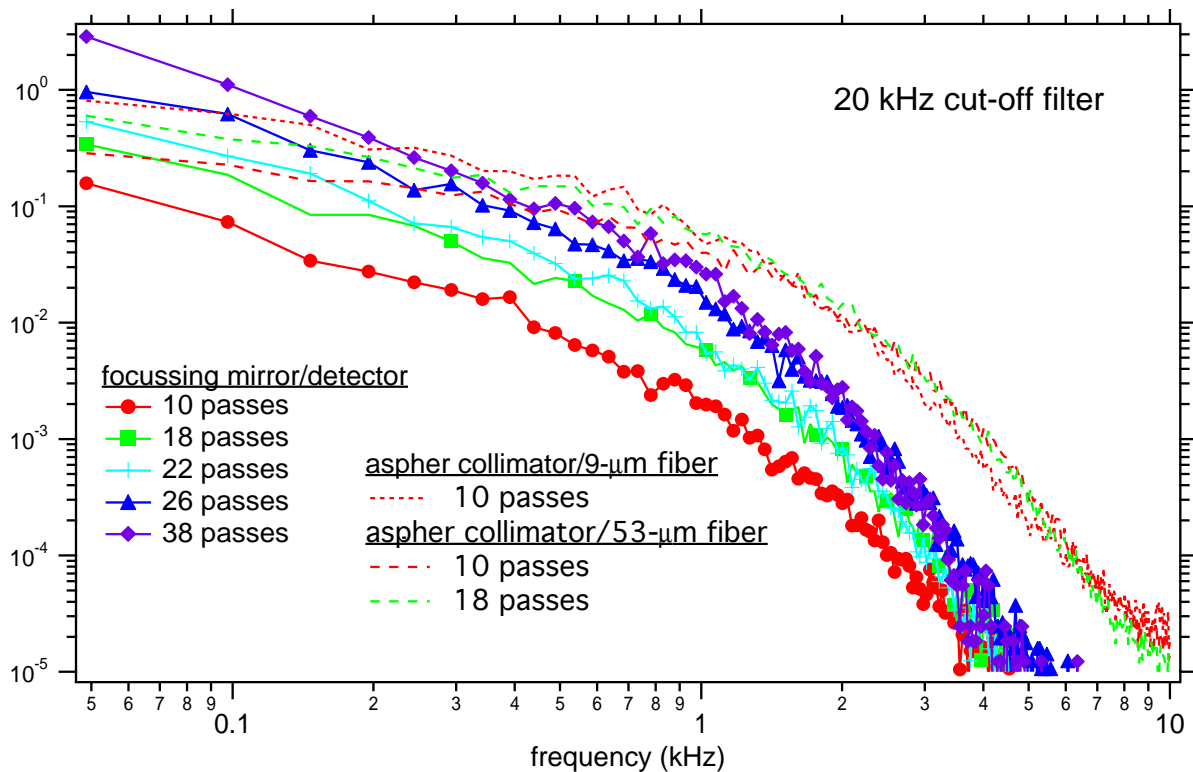


Figure 13. Power spectral densities of the transmitted TDL light as a function of Herriott cell passes and light collection methodology.

and numbers of optical passes. The actual separation of the Herriott mirrors changes slightly in order to achieve the different numbers of passes. The PSDs are calculated by taking the fast Fourier transform (FFT) of the measured first harmonic of the modulated laser ramp. The signal from the lock-in amplifier is low-pass filtered (at 20 kHz) prior to FFT analysis.

These tests generally show similar spectral response as a function of the number of laser passes in the Herriott cell and whether collecting the transmitted beam onto a single-mode (9- μm core) or multimode fiber (53- μm core). The higher PSD levels at lower frequencies that are apparent for more optical passes probably is a reflection of the higher fluctuation intensities one would expect with more optical passes through a given inhomogeneous probe volume. The high frequency tail in the fiber-collected data is most likely a reflection of higher detector noise level for the fiber-mounted detector used for those measurements, in comparison to the low-noise detector used for the direct detection measurements. One surprising aspect of these measurements is the significant fluctuation intensities seen all the way to 1 kHz in this small unsteady flame.

Beam-Steering

The effect of beam steering on the measured signal strength was evaluated for the same detection options discussed above, but using a non-sooty flame. The results of this investigation are concisely presented in Fig. 14, where the fraction of time that the laser transmittance is above a given value is plotted as a function of that given value. This plot demonstrates the increased light losses from beam steering that occurs as the number of optical passes increases in the Herriott cell, and as one progresses from direct detection onto a detector to collection onto a multimode fiber, or, as a worst case, onto a single-mode fiber. The effect of the number of optical passes on the

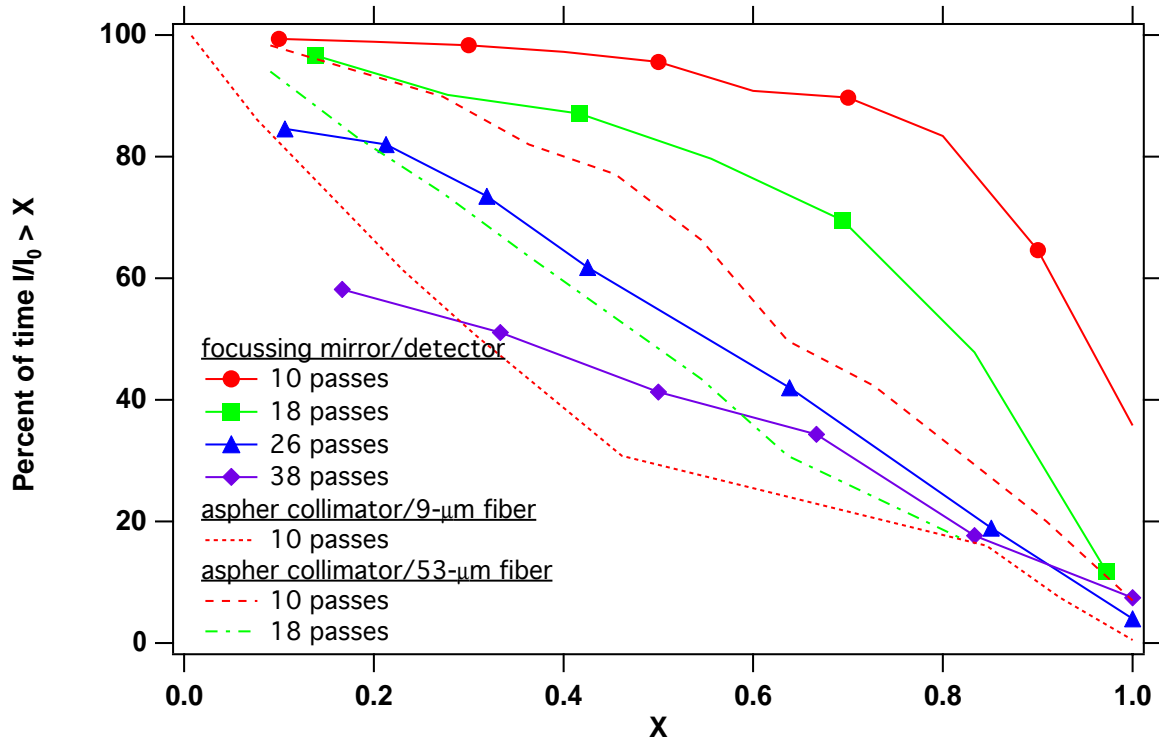


Figure 14. Effect of beam steering on transient laser transmittance in an unsteady, buoyant nonsooty diffusion flame.

average light transmission is seen in Fig. 15. It is clear from this plot that beam steering losses become particularly pronounced when more than 18 passes are used.

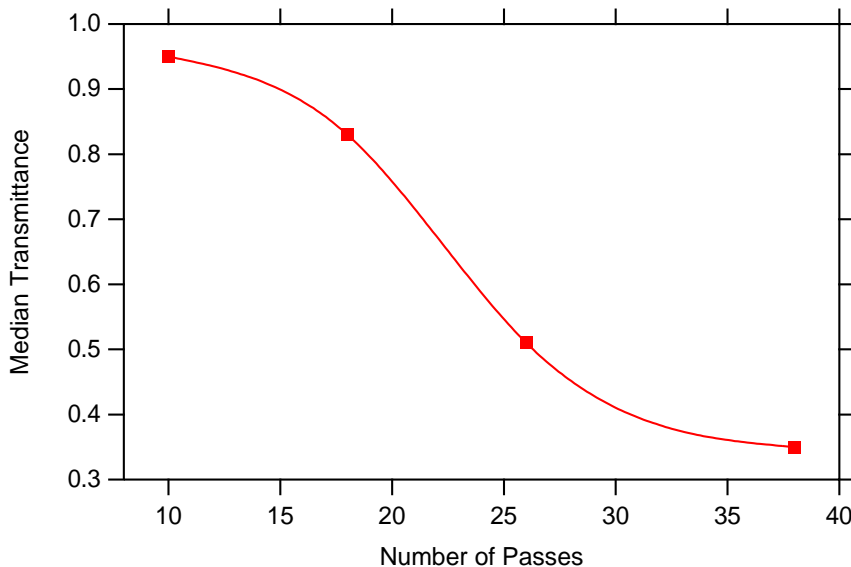


Figure 15. Power spectral densities of the transmitted TDL light as a function of Herriott cell passes and light collection methodology.

Large Fire Probe Design

Having determined that performing *in situ* multipassing using a Herriott cell mirror design is reasonably successful for TDL measurements in unsteady buoyant flames, at least up to 18 passes, a water-cooled, nitrogen-purged probe design was required to house the necessary optics for the measurements and to maintain the alignment between the two mirrors making up the sampling cell cavity. Because the previous fiber-coupled probe design had worked well in large fires (Gritz et al., 1998a), we based our new probe design on the basic geometry of that probe, wherein a single support arm branches out onto two facing arms within which the optical components are housed (see Fig. 16). However, our initial application was to make measurements in the FLAME facility, which requires that the probe be mounted from the side of the liquid pan, in contrast to the upright mounting used for large fire probes. As a consequence, the main arm length of the probe was determined by the necessary length to reach the center of the pool in FLAME, and the mounting design philosophy was to bring the probe in high over the fire and then to drop the diagnostic portion of the probe into the flame position of interest (thereby minimizing the disturbance to the flow at the actual optical sampling point). In general, one would like to minimize the separation of the two arms in order to promote alignment stability during the fire testing, as the probe heats up. However, the full bulk of the probe should also be suitably removed from the actual sampling volume to minimize any local flow disturbances. These considerations were balanced in our design, together with considerations of the necessary separation distance of the Herriott cell mirrors for the sizes and numbers of passes that we desired. The final design of the probe gave it a horizontal length of 43 inches, a vertical drop of 30 inches, a probe arm separation of 17 inches, and an arm standoff distance of 5 inches. Several steel endplates were manufactured with sight

tubes that screw onto the probe arm tips to yield actual physical sampling lengths that can vary from 3.6 to 7.5 cm.

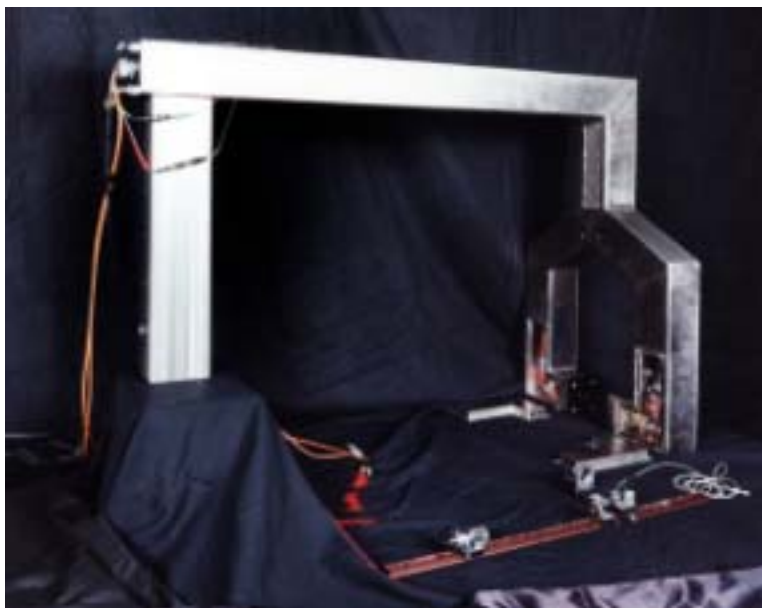


Figure 16. Photograph of the fiber-coupled, water-jacketed, nitrogen-purged diode laser sampling probe developed for measurements in large fires.

In order to maximize the water cooling available for the probe, it was designed with a water jacket between two concentric pieces of square aluminum tubing, 1/4-inch thick, with 2 1/2-inch and 3 1/2-inch OD. Eight ribs were tack brazed around the circumference of the inner tubing in order to provide good directionality to the cooling water flow. In order to provide access to the optical portion of the probe and the middle of the probe (for running fiber optics and thermocouple cables), o-ring seals were installed in the water jacket. These o-rings did not initially seal well, but after remachining of the mating surfaces and the installation of some shims, the probe has not had any subsequent leaks. The overall diameter of this probe is somewhat larger than the probe previously used at Sandia to support local optical measurements in pool fires, but it is hoped that with the improved cooling and the use of advanced ceramic insulation for this probe, its overall impact on the fire will be less than before.

The minimum mirror size that we felt comfortable using for the TDL Herriott cell in this first probe was 1-inch in diameter, and the brackets containing the fiber couplers were of a similar size, so we needed at least 2 inches in interior diameter in order to have room to adjust the alignment screws on the mini-mounts that were used to control the alignment of the optical components. In order to simplify alignment of the different components, the design incorporated small optical rails onto which the optical components were mounted. For simplicity of design and operation, collection of the transmitted TDL light onto a multimode fiber optic was used, although some additional optical loss is expected over the direct use of a detector element within the probe body. A photograph of a Herriott mirror and a fiber coupler mounted on an optical rail is shown in Fig. 17. Fig. 18 shows a photograph of the complete optical head portion of the probe. The mounting position of the Herriott cell mirrors was chosen in order to allow two sets of mirrors to be used, with 10 optical passes for one set of mirrors, and 18 passes for the other set.



Figure 17. Photograph of the Herriott cell mirror, mounting rail, and fiber coupler used in the optical probe.

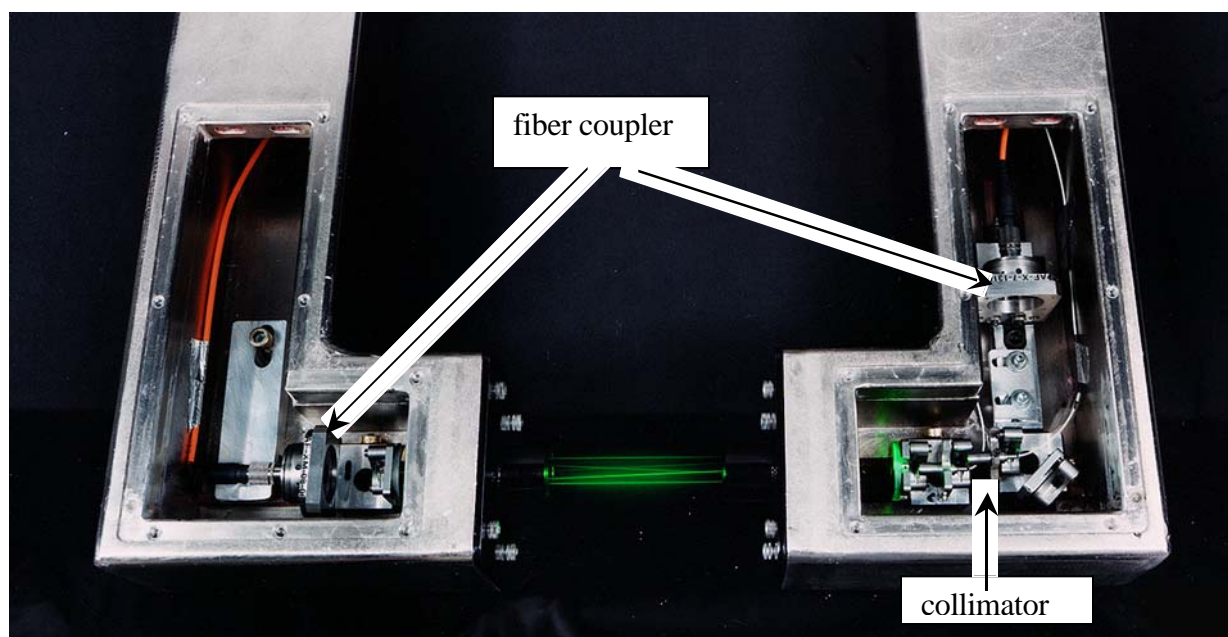


Figure 18. Photograph of the optical components within the sampling probe, with green laser light passing through the near-IR TDL optical system. Two small aspherical collimators launch the near-IR and red diode beams from the right side of the probe. The red beam passes along the centerline directly to the fiber coupler on the left side of the probe, whereas the near-IR beam reflects around the Herriott mirrors before exiting back out the right side, whereupon it is reflected around the elbow in the probe and captured via the fiber coupler to the upper right.

Large Fire Testing

Overview

The first planned testing series during May of 2000 at the FLAME facility of the Lurance Canyon Burn Site was canceled in the aftermath of the Cerro Grande fire in northern New Mexico, as severe fire restrictions were imposed. Once fire experiments were permitted at the Burn Site in late summer, a short duration sampling series was planned, starting with 1-ft pools of JP-8 (as an initial, soft test of the cooling capacity of the probe and the function of the optics) and then moving to 1-m and 2-m diameter pools. Photographs of the external appearance of the FLAME facility and of the TDL probe mounted in a 1-m pool fire are shown in Figs. 19 and 20. Three of the four desired TDLs had arrived for testing at the FLAME facility, but our electronics were limited to driving and locking-in on 2-laser systems, so we decided to focus our efforts on using the H₂O and C₂H₂ lasers.

Shipment and setup of the probe, fiber bundle, and TDL electronics proceeded without any difficulties, with the TDL optical alignment remaining perfectly intact during shipping and transport from the laboratory in Livermore to the Burn Site in Albuquerque. With the first test of the probe above a 1-ft pool, it was apparent that the probe insulation and the portable chiller cooling capacity were insufficient to the task, as the temperature within the probe rose to 130 deg. F. As a consequence, cooling water for the probe was routed through a large chiller being used to supply water to a large excimer laser at the Burn Site. However, even then the chiller had difficulty maintaining temperature in the probe, and when the first test was conducted in a 1-m pool fire, the chiller tripped in the middle of the burn, shutting off all flow to the probe. The maximum probe temperature recorded was 190 deg. F.

Problem Areas

Most of the optical transmission through the TDL optical system was lost when the probe interior reached temperatures so far above the design limit; transmission was only partially recovered when the probe returned to room temperature at the end of the fire. In subsequent 1-m fire tests, during which the probe reached approximately 160 deg F, the optical transmission through the TDL system continued to degrade. With limited time available to conduct the fire tests before the next experiment was scheduled to begin, the decision was made to continue to take the measurements in the fires, rather than taking the time to unwrap the insulation from the probe and to clean and realign the TDL optics.

The soot pyrometry measurement also did not perform well during this test series, because of the combined effects of unstable alignment on the APDs and because the test trailer temperature varied from 19 deg C in the morning to 38 deg C in the late afternoon, and the APD gain and offset are temperature-dependent. The alignment difficulty with the APDs was manifest because of the extremely small (0.5 mm diameter) detector elements used. The diode laser soot absorption measurement worked well throughout the test series.

Post-Mortem

At the completion of the fire test series, a total of 8 fires were investigated: 2 1-ft diameter fires and 6 1-m diameter fires, with measurements collected at various positions within the 1-m fires.

An attempt to calibrate the soot pyrometry system with a portable blackbody source revealed the difficulties in optical alignment and temperature drift of that system. Upon shipping the equipment back to Sandia/CA, a post-mortem of the optical probe revealed that the initial 30% optical throughput from the laser sources to the return fiber had been reduced to 2.5% throughput. The Herriott cell mirrors had a partial film of soot coating them. After cleaning with methanol, the optical throughput was 9%. A small adjustment of the turning mirror in the probe, which directs the transmitted beam to the output fiber coupler, restored the throughput to 30%, so it appears that no permanent damage was sustained by the optics due to the elevated temperatures they experienced.



Figure 19. Photograph of the Fire Laboratory for Accreditation of Models and Experiments (FLAME), at the Lurance Canyon Burn Site, Sandia National Labs, Albuquerque NM. The gray trailer on the left housed the two equipment racks for operation of the soot and species diagnostics, with a fiber optic bundle, cooling water lines, and thermocouple extension wires feeding from the back of the trailer into the enclosed facility.

Data Analysis

Analysis of the data collected at the end of FY00, at the end of the LDRD-funded project, occurred during the current fiscal year as part of an ESRF project focusing on soot measurements in fires.

The results of this analysis will be briefly presented here, in order to give the interested reader a flavor of the data that can now be collected with this newly developed diagnostic probe for pool fires.



Figure 20. Diode laser probe placed above a 1-m diameter JP-8 pool fire, shortly after ignition. When the fire reaches full development, its upper width is approximately twice that shown here, as is apparent from the soot deposition line on the overhead support section.

Various strategies, including performing single-color pyrometry were attempted to utilize the soot emission information that was collected, but in the end all were deemed to have failed. The red laser soot extinction measurements were interpreted in the classic manner, combining a Rayleigh-limit assumption regarding a negligible scattering/absorption ratio and the Dalzell and Sarofim (1969) reported soot index of refraction at 633 nm. Tunable diode laser signals of both water and acetylene (the two lasers that were used during the early portion of the testing) were found in the datafiles before the chiller failed and the probe lost significant optical throughput. A time series of water vapor and acetylene signals, together with soot volume fraction, is shown in Fig. 21. Interestingly, in many cases the water vapor and acetylene signals appear to be positively correlated, while the soot concentration tends to be negatively correlated with the gas species. One might expect various degrees of correlation of the different signals depending on whether the strongest soot signals are associated with its formation in the fuel-rich pyrolysis zone (where acetylene, but little water should be present) or with its presence in the quenched flame product gas (where some water but little acetylene should be present). The ~ 1.5 Hz puffing frequency for the 1-m pool is clearly evident in all of the time series data.

The time-averaged values of soot volume fraction at a given location within the 1-m fire are shown in Fig. 22 for various discrete sampling periods during the combustion history of the pool. It is apparent from these measurements that it takes over a minute for the fire to reach a steady state burning condition and that the fire only maintains steady state for an additional minute or two before slowly decaying. Finally, Fig. 23 shows power spectral density (PSD) functions of the

soot volume fraction from the individual datasets collected during the same 1-m fire as interrogated for the information in Figs. 21-22. The PSDs show good agreement with the Kolmogorov spectrum law (energy content $\propto f^{5/3}$) for isotropic, homogeneous turbulence (Hinze, 1959), up to ~ 300 Hz. Beyond this point, the PSDs decay faster than the $-5/3$ decay law.

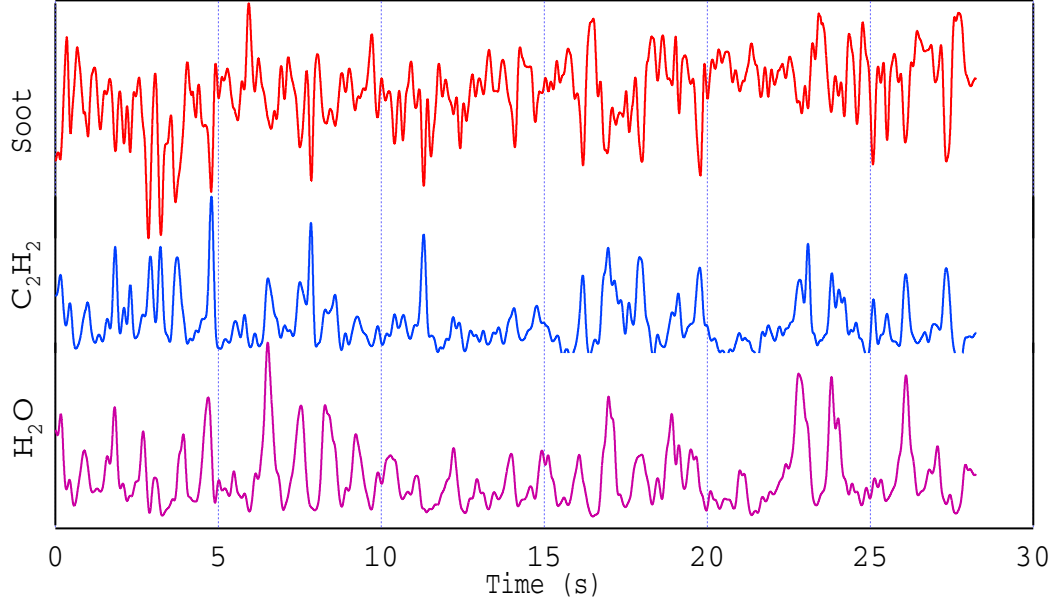


Figure 21. Time record of signals from TDL of water vapor and acetylene in a 1-m dia. JP-8 fire, combined with red laser extinction measurements of soot concentrations.

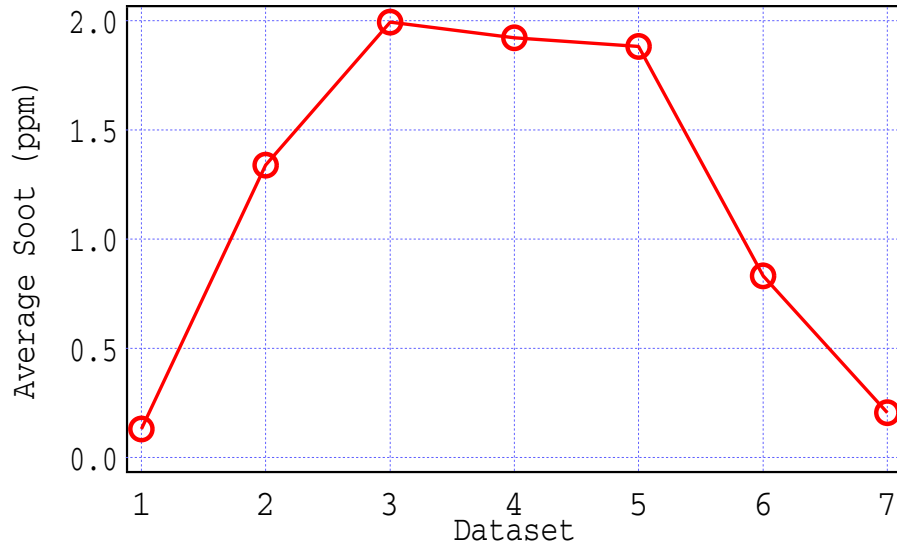


Figure 22. Time-averaged soot volume fractions deduced from discrete 25s-long datasets during the history of a 1-m dia. JP-8 pool fire.

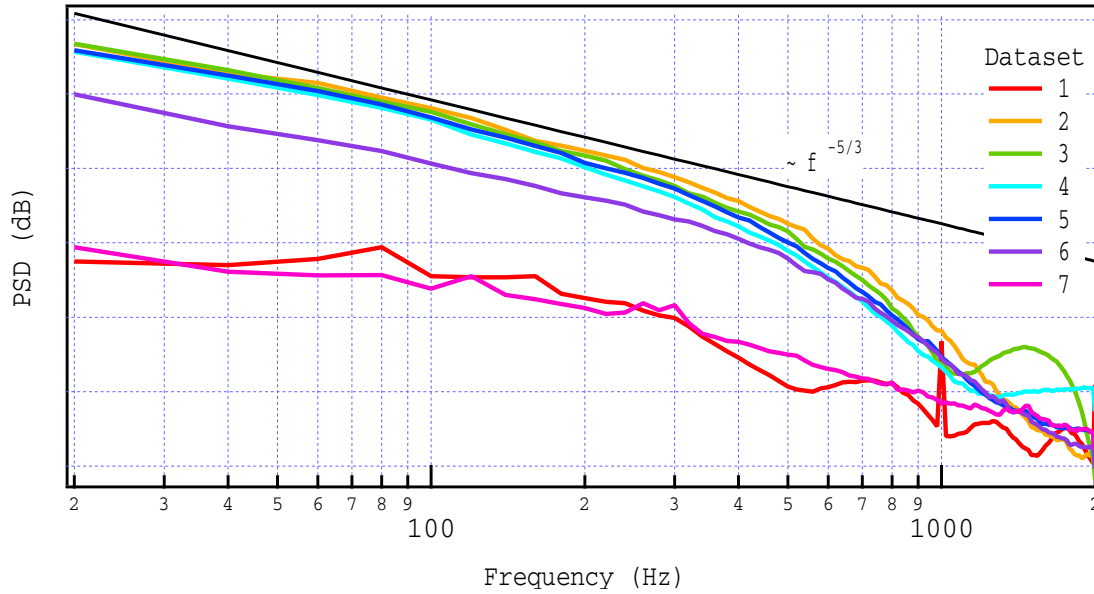


Figure 23. Power spectral density functions of soot concentration for different 25s-long datasets during the history of a 1-m dia. JP-8 pool fire.

Conclusions

This LDRD project has focused on the development of an integrated diagnostic technique for rapid measurements of gas species, soot concentrations, and soot temperature over a small sampling distance within large pool fires. Near-infrared tunable diode lasers were chosen as the best possible approach for making the gas species measurements. In order to improve the sensitivity of these measurements, an *in situ* multipassing arrangement was devised, using 1-inch dia. Herriott cell mirrors that have been drilled out to allow for incorporation of a variation of the classic 3-line soot absorption/emission measurement down the center of the TDL probe volume. Methane, acetylene, carbon monoxide, and water vapor were chosen to be the target gas species and suitable lasers were acquired. Multiplexing of these lasers was accomplished through the use of frequency domain multiplexing, incorporating custom built RF lock-in amplifiers with short time constants. Actual application of this system to pool fires at Sandia's FLAME facility at its Lurance Canyon Burn Site was limited to a single, initial trial, during which coolant system failures limited the extent of useful data collection. The data that was collected has some intriguing trends, suggesting that future use of this newly developed diagnostic technique in fires will yield a large amount of useful information.

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